

This Page Is Inserted by IFW Operations  
and is not a part of the Official Record

## **BEST AVAILABLE IMAGES**

Defective images within this document are accurate representations of the original documents submitted by the applicant.

Defects in the images may include (but are not limited to):

- BLACK BORDERS
- TEXT CUT OFF AT TOP, BOTTOM OR SIDES
- FADED TEXT
- ILLEGIBLE TEXT
- SKEWED/SLANTED IMAGES
- COLORED PHOTOS
- BLACK OR VERY BLACK AND WHITE DARK PHOTOS
- GRAY SCALE DOCUMENTS

**IMAGES ARE BEST AVAILABLE COPY.**

**As rescanning documents *will not* correct images,  
please do not report the images to the  
Image Problem Mailbox.**



PTO



Europäisches Patentamt  
European Patent Office  
Office européen des brevets

(11) Publication number:

**0 270 078**  
**A2**

(12)

## EUROPEAN PATENT APPLICATION

(21) Application number: 87117764.8

(51) Int. Cl. 4: G03C 1/78, G03C 7/32

(22) Date of filing: 01.12.87

(30) Priority: 02.12.86 JP 287456/86  
20.04.87 JP 95440/87

(43) Date of publication of application:  
08.06.88 Bulletin 88/23

(84) Designated Contracting States:  
DE FR GB NL

(71) Applicant: Fuji Photo Film Co., Ltd.  
210 Nakanuma Minamishigara-shi  
Kanagawa-ken(JP)

(72) Inventor: Aogaki, Yukio Fuji Photo Film Co., Ltd.

No. 210 Nakanuma  
Minamishigara-shi Kanagawa-ken(JP)

Inventor: Toda, Yuzo Fuji Photo Film Co., Ltd.

No. 210 Nakanuma  
Minamishigara-shi Kanagawa-ken(JP)

Inventor: Minagawa, Nobuhiko Fuji Photo Film Co., Ltd.

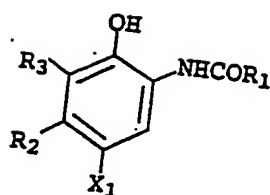
No. 210 Nakanuma  
Minamishigara-shi Kanagawa-ken(JP)

(74) Representative: Patentanwälte Grünecker,  
Kinkeldey, Stockmalr & Partner  
Maximilianstrasse 58  
D-8000 München 22(DE)

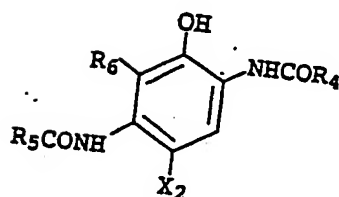
(54) Silver halide color photographic material and color photographic print.

(57) A silver halide color photographic material is described, comprising a reflective support composed of a vinyl chloride resin containing a white pigment and having thereon in an appropriate order at least one red-sensitive silver halide emulsion layer containing a cyan color forming coupler represented by the general formula (1) or (2) shown below, at least one green-sensitive silver halide emulsion layer containing a magenta color forming coupler represented by the general formula (3) or (4) shown below, and at least one blue-sensitive silver halide emulsion layer containing a yellow color forming coupler represented by the general formula (5) shown below

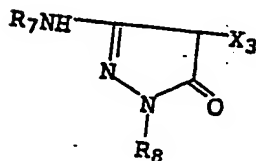
EP 0 270 078 A2



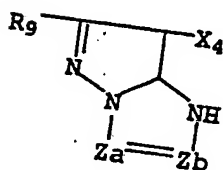
(1)



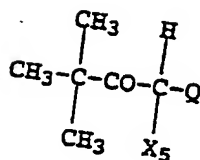
(2)



(3)



(4)



(5)

wherein  $R_1$ ,  $R_4$  and  $R_5$  each represents an aliphatic group, an aromatic group, a heterocyclic group, an aromatic amino group or a heterocyclic amino group;  $R_2$  represents an aliphatic group;  $R_3$  and  $R_6$  each represents a hydrogen atom, a halogen atom, an aliphatic group, an aliphatic oxy group or an acylamino group;  $R_7$  and  $R_8$  each represents a substituted or unsubstituted phenyl group;  $R_9$  represents a hydrogen atom or a substituent;  $R_2$  and  $R_3$  or  $R_5$  and  $R_6$  may be connected with each other to form a 5-membered to 7-membered ring;  $Q$  represents a substituted or unsubstituted N-phenylcarbonyl group;  $Za$  and  $Zb$ , which may be the same or different, each represents a group of  $-CH_2-$  a group of



or a group of  $-N=$ ;  $R_{10}$

represents the same substituent as that represented by  $R_9$ ; and  $X_1$ ,  $X_2$ ,

X<sub>3</sub>, X<sub>4</sub> and X<sub>5</sub> each represents a hydrogen atom or a group capable of being released upon a reaction with an oxidation product of an aromatic primary amine developing agent.

The silver halide color photographic material provides a color photographic print having color images of excellent sharpness and good smoothness.

A color photographic print comprising a reflective support composed of a vinyl chloride resin containing a white pigment and having thereon in an appropriate order at least one emulsion layer containing a cyan dye obtained by a reaction of a cyan color forming coupler represented by the general formula (1) or (2) shown above with an oxidation product of an aromatic primary amine developing agent (CD), at least one emulsion layer containing a magenta dye obtained by a reaction of a magenta color forming coupler represented by the general formula (3) or (4) shown above with a CD, and at least one emulsion layer containing a yellow dye obtained by a reaction of a yellow color forming coupler represented by the general formula (5) shown above with a CD is also described.

SILVER HALIDE COLOR PHOTOGRAPHIC MATERIAL  
AND COLOR PHOTOGRAPHIC PRINT

FIELD OF THE INVENTION

The present invention relates to a silver halide color photographic material and a color photographic print, and more particularly to a color photographic print suitable for use as an ID card, a cashing card, a telephone card, etc.

BACKGROUND OF THE INVENTION

Conventional silver halide color photographic materials comprise a silver halide emulsion layer containing a cyan color forming coupler, a silver halide emulsion layer containing a magenta color forming coupler and a silver halide emulsion layer containing a yellow color forming coupler coated on various kinds of supports.

It is known that as a light transmissive photographic support, a transparent plastic film, for example, a cellulose triacetate film, a polyethylene terephthalate film, a vinyl resin film, etc. may be employed, and as a reflective support, baryta coated paper, synthetic paper, polyethylene laminated paper, a plastic sheet containing a white pigment, a glass plate, a metal plate (for example, an aluminium plate having an anodized surface), etc. may be employed.

With respect to reflective supports, it has been proposed that a white pigment be incorporated into a

plastic material or that a white pigment containing layer is provided on a surface of a plastic material in order to particularly improve whiteness of the supports.

However, when whiteness of a support is increased, while reproducibility of a white object is improved, sharpness of images usually rather tends to decrease due to reflection during exposure, halation, etc. Therefore, attempts have been made to incorporate an irradiation preventing dye into a light-sensitive silver halide emulsion layer provided on the support or to apply an antihalation layer to the support.

Further, when baryta coated paper or polyethylene laminated paper is employed as a support, smoothness of the support is poor due to unevenness of paper fiber and thus uneven thickness of a silver halide emulsion layer occurs, resulting in a severe problem with irregularity of image density obtained after development processing.

Such a problem is particularly noticeable when a sky scene is photographed and especially when it is photographed in color.

#### SUMMARY OF THE INVENTION

Therefore, an object of the present invention is to provide a reflective color photographic light-sensitive material which forms color images having improved sharpness and a color photographic print which has color images of improved sharpness.

Another object of the present invention is to provide a silver halide color photographic material and a color photographic print each having a reflective support of good smoothness.

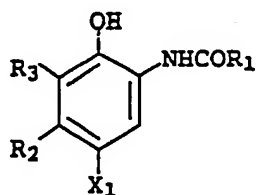
Still another object of the present invention is to provide a support as used for a silver halide color photographic material and a color photographic print on the surface of which a figure, a letter, etc. can be subjected to embossment with heat processing when the material or the print is used as various kinds of cards.

Other objects of the present invention will become apparent from the following detailed descriptions and examples.

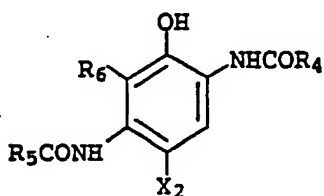
As the results of extensive investigation, it has been found that the above-described objects can be effectively achieved by a silver halide color photographic material comprising a reflective support composed of a vinyl chloride resin containing a white pigment and having thereon in an appropriate order at least one red-sensitive silver halide emulsion layer containing a cyan color forming coupler represented by the general formula (1) or (2) shown below, at least one green-sensitive silver halide emulsion layer containing a magenta color forming coupler represented by the general formula (3) or (4) shown below, and at least one blue-sensitive silver halide emulsion layer containing a yellow color forming coupler



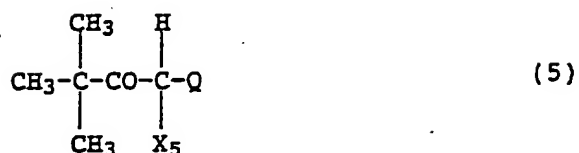
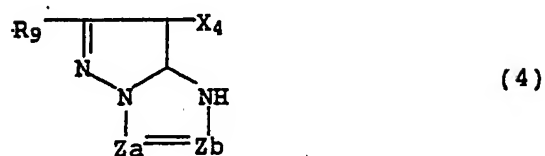
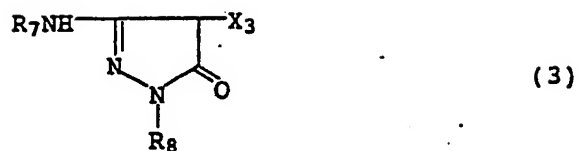
represented by the general formula (5) shown below and also with a color photographic print comprising a reflective support composed of a vinyl chloride resin containing a white pigment and having thereon in an appropriate order at least one emulsion layer containing a cyan dye obtained by a reaction of a cyan color forming coupler represented by the general formula (1) or (2) shown below with an oxidation product of an aromatic primary amine developing agent (hereinafter referred to as "CD"), at least one emulsion layer containing a magenta dye obtained by a reaction of a magenta color forming coupler represented by the general formula (3) or (4) shown below with a CD, and at least one emulsion layer containing a yellow dye obtained by a reaction of a yellow color forming coupler represented by the general formula (5) shown below with a CD.



(1)



(2)



wherein R<sub>1</sub>, R<sub>4</sub> and R<sub>5</sub> each represents an aliphatic group, an aromatic group, a heterocyclic group, an aromatic amino group or a heterocyclic amino group; R<sub>2</sub> represents an aliphatic group; R<sub>3</sub> and R<sub>6</sub> each represents a hydrogen atom, a halogen atom, an aliphatic group, an aliphatic oxy group or an acylamino group; R<sub>7</sub> and R<sub>8</sub> each represents a substituted or unsubstituted phenyl group; R<sub>9</sub> represents a hydrogen atom or a substituent; R<sub>2</sub> and R<sub>3</sub> or R<sub>5</sub> and R<sub>6</sub> may be connected with each other to form a 5-membered to 7-membered ring; Q represents a substituted or unsubstituted N-phenylcarbamoyle group; Z<sub>a</sub> and Z<sub>b</sub>, which may be the same or different, each represents a group of -CH=, a

group of  $\overset{R_{10}}{\underset{|}{-C=}}$  or a group of  $-N=$ ;  $R_{10}$  represents the same substituent as that represented by  $R_9$ ; and  $X_1$ ,  $X_2$ ,  $X_3$ ,  $X_4$  and  $X_5$  each represents a hydrogen atom or a group capable of being released upon a reaction with a CD.

#### DETAILED DESCRIPTION OF THE INVENTION

The color photographic print according to the present invention includes a color photographic print obtained by conducting at least a step of processing the silver halide color photographic material of the present invention, after imagewise exposure, with a color developing solution containing an aromatic primary amine color developing agent, and a color photographic print obtained by adhering the above-described color photographic print (but employing a transparent support) on a reflective support composed of a vinyl chloride resin containing a white pigment.

In the general formula (1), (2), (3), (4) or (5), the group capable of being released represented by  $X_1$ ,  $X_2$ ,  $X_3$ ,  $X_4$  or  $X_5$  include those as described in U.S. Patent 4,540,654, column 4, line 30 to column 5, line 24, herein incorporated by reference. Among them, a chlorine atom for  $X_1$  or  $X_2$ , a hydrogen atom or a group capable of being released containing a sulfur atom as a releasing atom for  $X_3$  or  $X_4$  and a group capable of being released containing

an oxygen atom or a nitrogen atom as a releasing atom for X<sub>5</sub> are preferred.

Now, the reflective support which can be employed in the present invention will be explained in detail below.

The vinyl chloride resin which constitutes the reflective support used in the present invention is a homopolymer or copolymer containing a vinyl chloride monomer as at least one kind of monomers. It is preferred that the vinyl chloride monomer occupies at least 50% by weight of the total monomer component. Suitable examples of comonomer component include, for example, methyl methacrylate, vinyl acetate, acrylonitrile, a fluorinated olefin, a vinyl ether, vinyl bromide, vinyl acetate, maleic acid, dichlorobutadiene, vinyl fluoride, vinylidene fluoride, trifluorochloroethylene, tetrafluoroethylene, vinylidene chloride, acrylonitrile, styrene, butadiene, chloroprene, etc. Two or more of these comonomer components may be employed.

To the vinyl chloride resin may be added various fillers, plasticizers and stabilizers. Suitable examples of fillers include starch, wood flour, clay, calcium carbonate, bentonite, etc. Suitable examples of plasticizers include a phthalic ester (e.g., dibutyl phthalate, dioctyl phthalate, dicyclohexyl phthalate, di-2-ethylhexyl phthalate, butyllauryl phthalate, dilauryl phthalate,

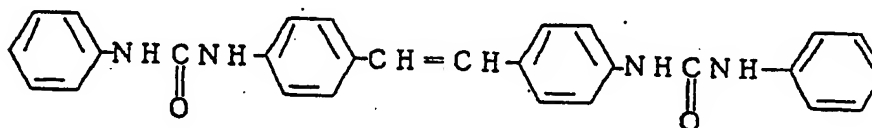
butylbenzyl phthalate), a phosphoric ester (e.g., tricresyl phosphate, trixylenyl phosphate, trioctyl phosphate), a straight chain dibasic acid ester (e.g., dioctyl adipate, dioctyl azelate, dioctyl sebacate), butylphthalyl butylglycolate, etc. Suitable examples of stabilizers include tribasic lead sulfate, dibasic lead stearate, lead orthostearate, etc.

Filler may be added in an amount of from about 20 parts to 100 parts by weight per 100 parts by weight of the resin material.

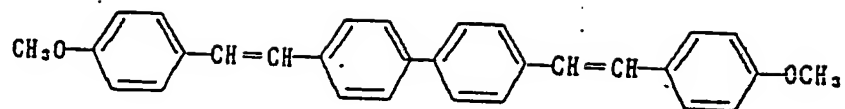
The white pigments which can be added to the vinyl chloride resin include titanium white, zinc white, calcium carbonate, barium sulfate, white lead, white organic pigments or dyes, brightening agents, etc.

Preferred examples of the aforementioned brightening agents include the following compounds.

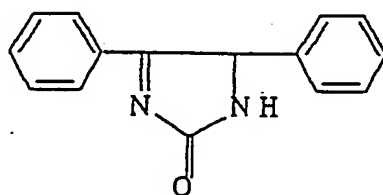
Compound (1)



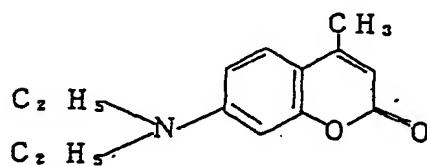
Compound (2)



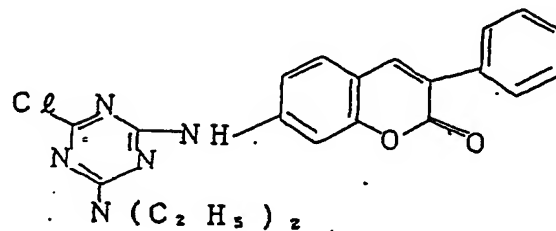
Compound (3)



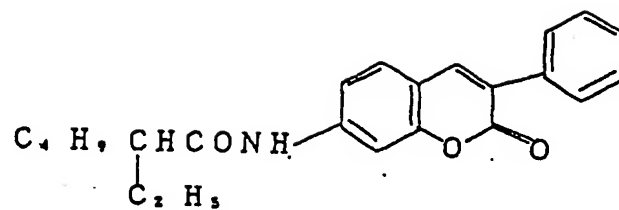
Compound (4)



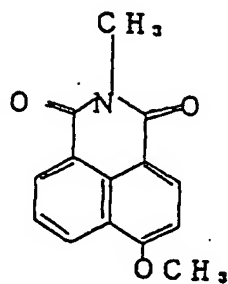
Compound (5)



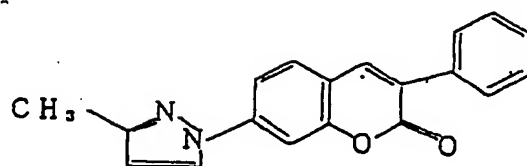
Compound (6)



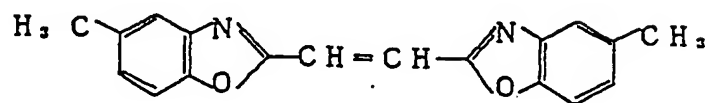
Compound (7)



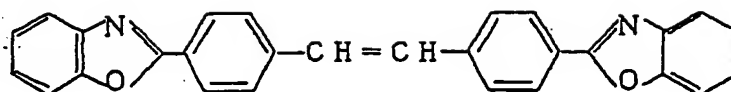
Compound (8)



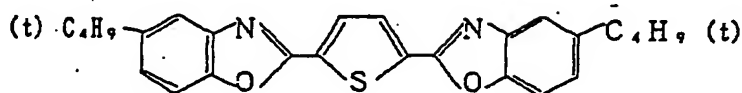
Compound (9)



Compound (10)



Compound (11)



The white pigments can be employed individually or as a mixture of two or more thereof. The total amount of the white pigment added is preferably from 1 part by weight to 30 parts by weight and more preferably from 5 parts by weight to 15 parts by weight per 100 parts by weight of the vinyl chloride resin material.

The vinyl chloride resin as used in the present invention exhibits resistance to heat deformation, preferably to at least 50°C, more preferably to at least 70°C from the standpoint of preventing a dimensional change during the drying step after preparation and development steps of light-sensitive materials or during use thereof.



It is preferred that an average reflectivity of the reflective support used in the present invention in a visible range is from 80 to 98%.

The thickness of the reflective support is preferably from 50  $\mu\text{m}$  to 500  $\mu\text{m}$  and more preferably from 100  $\mu\text{m}$  to 300  $\mu\text{m}$ .

When a hydrophilic colloid layer such as a silver halide emulsion layer is coated on the reflective support, a subbing treatment may be conducted in order to improve adhesion of both materials. With respect to the subbing treatment, various kinds of methods are known and a suitable method can be appropriately selected therefrom.

For instance, there may be employed a method wherein a surface of a support is etched with acetone to make a rough surface, wood flour (cellulose component) is coated to fill in a concave portion of the surface and to cover a convex portion of the surface and thereby an affinity with gelatin is provided (because of a good affinity between cellulose and protein) and then a subbing solution containing pearl essence is coated thereon as described in Japanese Patent Publication No. 3583/60, a method wherein at least one layer composed of a mixture of cellulose nitrate and a vinyl acetate-vinyl chloride copolymer is coated as a subbing agent as described in Japanese Patent Publication No. 25742/64, a method wherein a support is subjected to corona discharge treatment to a

specified degree and then a layer containing a hydrophilic colloidal binder (such as gelatin) and dispersible colloidal silica at a weight ratio of 5/1 to 1/2 is coated thereon as described in European Patent Application (OPI) No. EP 0065329A1 (the term "OPI" as used herein refers to a "published unexamined application"), a method wherein a straight chain polyphosphoric acid ester resin is coated on a support as described in British Patent 742,370, a method wherein a hardened gelatin subbing layer is subjected to corona discharge treatment and then a light-sensitive silver halide emulsion layer is coated as described in British Patent 1,472,854, a method wherein an epoxidated rubbery polymer and a film-forming unsaturated polyester are coated as subbing agents as described in British Patent 1,179,563, a method wherein first a solution of a isobutyl methacrylate polymer dissolved in a solvent which does not affect a vinyl chloride polymer and then a usual subbing layer composed of gelatin and cellulose nitrate is coated thereon as described in U.S. Patent 2,388,817, and a method wherein a subbing solution having the composition shown below is coated on a support as described in U.S. Patent 2,483,966.

<u>Composition of Subbing Solution</u>	<u>Parts by Weight</u>
Cellulose Nitrate (nitrogen content 11%)	5.0 to 7.0
Acetone	40.0 to 50.0
Methyl Ethyl Ketone	9.0 to 10.0
Methanol	25.0 to 35.0
Diethyl Phosphate	2.5 to 4.2
Ethanol	0.0 to 3.5

It is preferred that a development inhibitor releasing compound (DIR compound) is added to the color photographic light-sensitive material according to the present invention for the purpose of further improving sharpness.

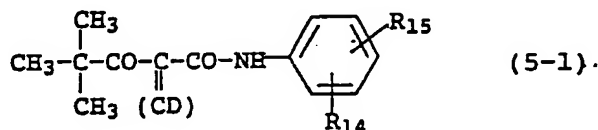
Suitable DIR compounds include DIR couplers as described in U.S. Patents 3,933,500, 4,187,100 and 4,477,563, British Patent 1,504,094 and Japanese Patent Application (OPI) Nos. 206834/84, 210440/84 and 92556/85.

Now, the dye which is formed upon a coupling reaction of the color image forming coupler represented by the above-described general formula (1), (2), (3), (4) or (5) which is used in the present invention with an oxidation product of an aromatic primary amine color developing agent (CD) will be explained in greater detail below.

Of yellow dyes, dyes formed from pivaloyl acetanilide type couplers are preferred. These dyes have excellent features that the long wavelength side of their

spectral absorptions is sharply cut and that their fastness is excellent. Further, they are easily dispersed in a hydrophilic colloid using a small amount of an organic solvent or using a water-insoluble and organic solvent soluble polymer, in comparison with benzoyl acetanilide type couplers, and thus they enable provision of a color-forming layer which is thin and has strong physical property.

The yellow dyes which are preferably employed in the present invention are those represented by the following general formula (5-1):

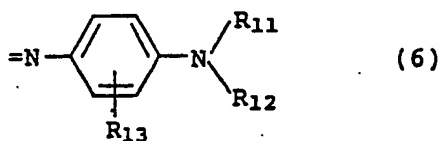


wherein  $\text{R}_{14}$  and  $\text{R}_{15}$ , which may be the same or different, each represents a hydrogen atom or a substituent which is ordinarily used for a yellow coupler, provided that both  $\text{R}_{14}$  and  $\text{R}_{15}$  are not hydrogen atoms at the same time; and  $\text{(CD)}$  represents a coupling residue of an aromatic primary amine developing agent.

Suitable examples of the substituents represented by  $\text{R}_{14}$  and  $\text{R}_{15}$  include an alkyl group, an alkenyl group, an alkoxy group, an alkoxycarbonyl group, a halogen atom, an alkoxycarbamoyl group, an aliphatic amido group, an alkylsulfamoyl group, an alkylsulfonamido group, an

alkylureido group, an alkyl-substituted succinimido group, an aryloxy group, an aryloxy carbonyl group, an arylcarbamoyle group, an arylamido group, an arylsulfamoyl group, an arylsulfonamide group, an arylureido group, a carboxy group, a sulfo group, a nitro group, a cyano group, a thiocyno group, etc. The coupler used may be a polymer coupler including a bis coupler, among others.

In the general formula (5-1), (CD) preferably represents a coupling residue of a phenylenediamine derivative represented by the following general formula (6):

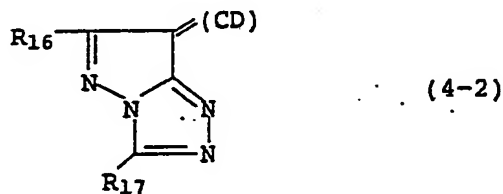
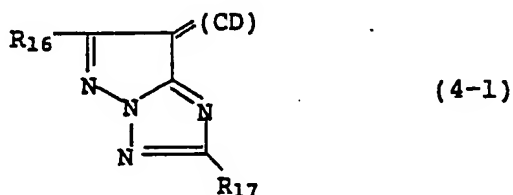


wherein  $R_{11}$  and  $R_{12}$  each represents a substituted or unsubstituted alkyl group; and  $R_{13}$  represents one to four hydrogen atoms or one to four substituents.

In the general formula (6), the alkyl group represented by  $R_{11}$  or  $R_{12}$  is preferably an alkyl group having from 1 to 4 carbon atoms. Suitable examples of the substituents for the alkyl group include a hydroxy group, an alkylsulfonamido group, an alkoxy group, etc. Specific examples of  $R_{11}$  or  $R_{12}$  include an ethyl group, a  $\beta$ -hydroxyethyl group, a  $\beta$ -methanesulfonamidoethyl group, a  $\beta$ -methoxyethyl group, etc. Further, a representative

example of the substituent represented by  $R_{13}$  is an alkyl group (for example, a methyl group, etc.).

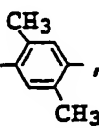
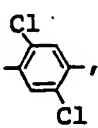


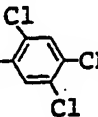
As the magenta dyes used in the present invention, those represented by the following general formula (4-1) or (4-2) are preferred.






wherein  $(CD)$  represents a coupling residue of an aromatic primary amine developing agent and  $R_{16}$  and  $R_{17}$ , which may be the same or different, each represents a hydrogen atom, a halogen atom, an alkyl group, an aryl group, a heterocyclic group, a cyano group, an alkoxy group, an aryloxy group, a heterocyclic oxy group, an acyloxy group, a carbamoyloxy group, a silyloxy group, a sulfonyloxy group, an acylamino group, an anilino group, a ureido group, an imido group, a sulfamoylamino group, a carbamoylamino group, an alkylthio group, an arylthio

group, a heterocyclic thio group, an alkoxycarbonylamino group, an aryloxycarbonylamino group, a sulfonamido group, a carbamoyl group, an acyl group, a sulfamoyl group, a sulfonyl group, a sulfinyl group, an alkoxycarbonyl group or an aryloxycarbonyl group. Of these groups, an alkyl group, an alkoxy group, an alkylthio group, an aryl group, an aryloxy group, an arylthio group, an acylamino group and an anilino group are particularly preferred. Also,  $R_{16}$  or  $R_{17}$  may be a divalent group to form a bis compound. Further, the magenta dye represented by the general formula (4-1) or (4-2) may be in the form of a polymer dye in which the dye moiety represented by the general formula (4-1) or (4-2) exists at the main chain or the side chain of the polymer and particularly a polymer derived from a vinyl monomer having the moiety represented by the general formula (4-1) or (4-2) is preferred. In this case,  $R_{16}$  or  $R_{17}$  represents a linking group connected to a vinyl group.

The linking group represented by  $R_{16}$  or  $R_{17}$  in the cases wherein the part represented by the general formula (4-1) or (4-2) is included in a vinyl monomer includes an alkylene group (including a substituted or unsubstituted alkylene group, e.g., a methylene group, an ethylene group, a 1,10-decylene group,  $-\text{CH}_2\text{CH}_2\text{OCH}_2\text{CH}_2-$ , etc.), a phenylene group (including a substituted or unsubstituted phenylene group, e.g., a 1,4-phenylene group, a 1,3-

phenylene group, , , etc.) -NHCO-, -CONH-,  
 -O-, -OCO-, and an aralkylene group (e.g., -CH<sub>2</sub>--CH<sub>2</sub>-,  
 -CH<sub>2</sub>CH<sub>2</sub>--CH<sub>2</sub>CH<sub>2</sub>-, -CH<sub>2</sub>--CH<sub>2</sub>-, etc.) or a combination  
 thereof.

Specific examples of preferred linking groups  
 include -NHCO-, -CH<sub>2</sub>CH<sub>2</sub>-, -CH<sub>2</sub>CH<sub>2</sub>CH<sub>2</sub>--NHCO-, -NHCO-,  
 -CH<sub>2</sub>CH<sub>2</sub>NHCO-, -CH<sub>2</sub>CH<sub>2</sub>-O-C(=O)-, -CONHCH<sub>2</sub>CH<sub>2</sub>NHCO-,  
 -CH<sub>2</sub>CH<sub>2</sub>OCH<sub>2</sub>CH<sub>2</sub>NHCO-, and -CH<sub>2</sub>CH<sub>2</sub>--CH<sub>2</sub>CH<sub>2</sub>NHCO-.

Further, a vinyl group in the vinyl monomer may  
 further have a substituent in addition to the moiety  
 represented by the general formula (4-1) or (4-2).  
 Preferred examples of these substituents include a  
 chlorine atom or a lower alkyl group having from 1 to 4  
 carbon atoms (e.g., a methyl group, an ethyl group, a  
 butyl group, etc.).

The polymer derived from a vinyl monomer having  
 the dye moiety may be a copolymer with a non-color forming  
 ethylenic monomer.

Suitable examples of the non-color forming  
 ethylenic monomers include an acrylic acid such as acrylic  
 acid,  $\alpha$ -chloroacrylic acid,  $\alpha$ -alacrylic acid (e.g.,



methacrylic acid, etc.), etc., an ester or an amide derived from an acrylic acid (e.g., acrylamide, n-butylacrylamide, tert-butylacrylamide, diacetoneacrylamide, methacrylamide, methyl acrylate, ethyl acrylate, n-propyl acrylate, n-butyl acrylate, tert-butyl acrylate, isobutyl acrylate, 2-ethylhexyl acrylate, n-octyl acrylate, vinyl propionate, vinyl laurate, etc.), acrylonitrile, methacrylonitrile, an aromatic vinyl compound (e.g., styrene and a derivative thereof, vinyltoluene, divinylbenzene, vinylacetophenone, sulfostyrene, etc.), itaconic acid, citraconic acid, crotonic acid, vinylidene chloride, a vinyl alkyl ether (e.g., vinyl ethyl ether etc.), maleic acid, maleic anhydride, a maleic acid ester, N-vinyl-2-pyrrolidone, N-vinylpyridine, 2- or 4-vinylpyridine, etc. Particularly, an acrylic acid ester, a methacrylic acid ester and a maleic acid ester are preferred.

Two or more non-color forming ethylenically unsaturated monomers can be used together. For example, a combination of n-butyl acrylate and methyl acrylate, styrene and methacrylic acid, methyl acrylate and diacetoneacrylamide, etc. can be used.

As is well known in the field of polymer color couplers, the non-color forming ethylenically unsaturated monomer which is used to copolymerize with a solid water-insoluble monomer coupler can be selected in such a manner

that the copolymer to be formed has good physical properties and/or chemical properties, for example, solubility, compatibility with a binder in a photographic colloid composition such as gelatin, flexibility, heat stability, etc.

The magenta dyes according to the present invention are characterized by a good spectral absorption characteristic wherein the characteristic second absorption on the short wavelength side is not present or, if present, is small and the absorption on the long wavelength side is sharply cut, and in excellent fastness to high humidity and heat. Further, in the case of using polymer magenta dyes, they can be dispersed as a latex and thus an organic solvent having a high boiling point is not necessary, or is used only in a reduced amount. As the result, it is possible to decrease the thickness of the color forming layer and to increase the physical strength thereof.

The cyan dyes used in the present invention are most typically dyes which are obtained upon an oxidation coupling reaction of phenol type couplers with paraphenylenediamine color developing agents. These phenol type cyan couplers may be used together with naphthol type cyan couplers. Specific examples of naphthol type couplers include those as described, for example, in U.S. Patent 2,474,293 and preferably those as described, for example,

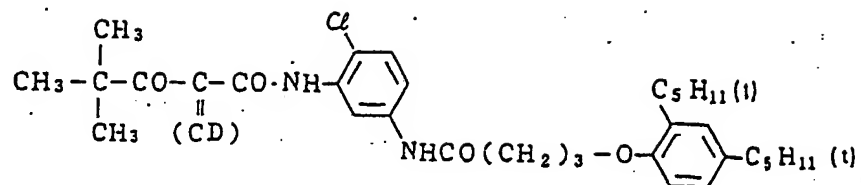
in U.S. Patents 4,052,212, 4,146,396, 4,228,233 and 4,296,200. Specific examples of phenol couplers include those as described, for example, in U.S. Patents 2,396,929, 2,801,171 2,772,162 and 2,895,826.

Cyan couplers which are stable against humidity and temperature are advantageously used in the present invention. Typical examples of these couplers include phenol cyan couplers having an alkyl group more than a methyl group at the meta-position of the phenol nucleus as described in U.S. Patent 3,772,002, cyan couplers as described in U.S. Patents 2,772,162, 3,758,308, 4,126,396, 4,334,011 and 4,327,173, West German Patent Application (OLS) No. 3,329,729 and European Patent 121,365, etc., and cyan couplers as described in U.S. Patents 3,446,622, 4,333,999, 4,451,559 and 4,427,767, etc.

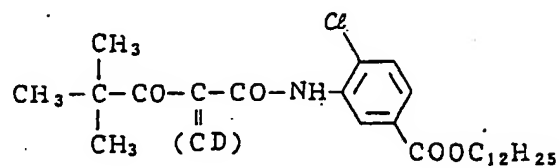
The cyan dyes according to the present invention can cover a wavelength range of 600 mμ to 700 mμ by using two or more dyes represented by the general formula (1) or (2) in combination. The cyan dyes have good features that they provide cyan color images having small absorption on the short wavelength side and that they are excellent in fastness to high humidity and heat.

Specific examples of the dyes which can be used in the present invention are set forth below, but the present invention should not be construed as being limited thereto.

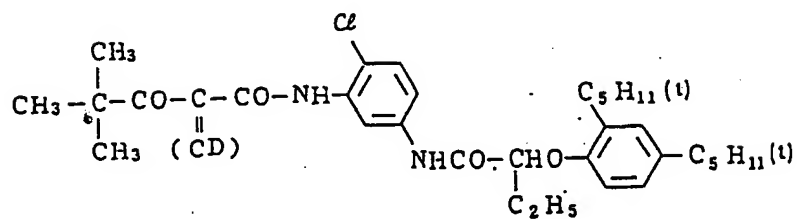
(1)-1



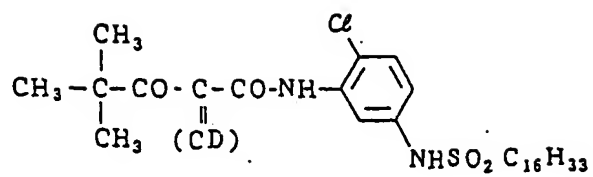
(1)-2



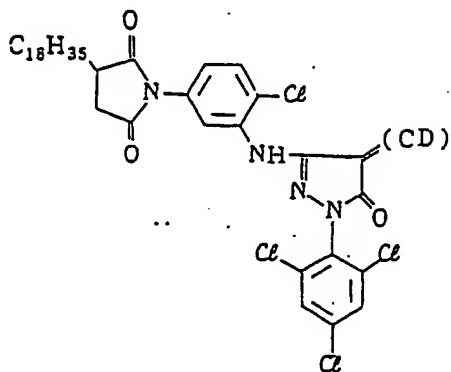
(1)-3



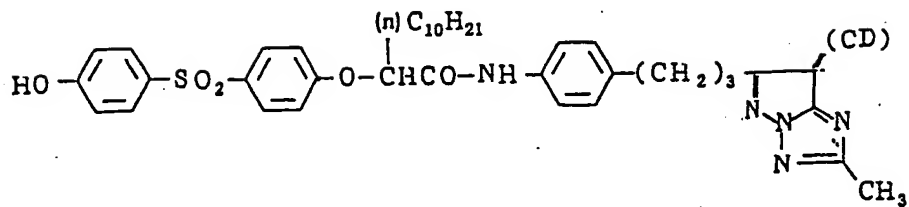
(1)-4



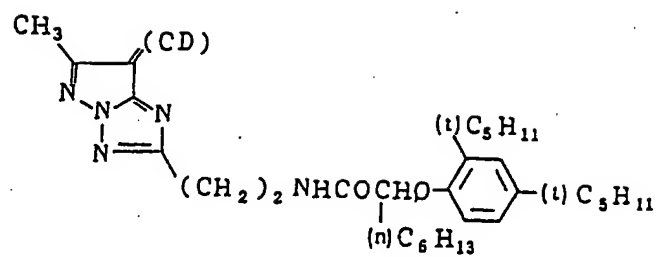
(2)-1



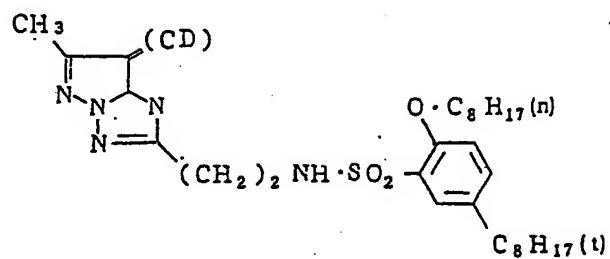
(2)-2



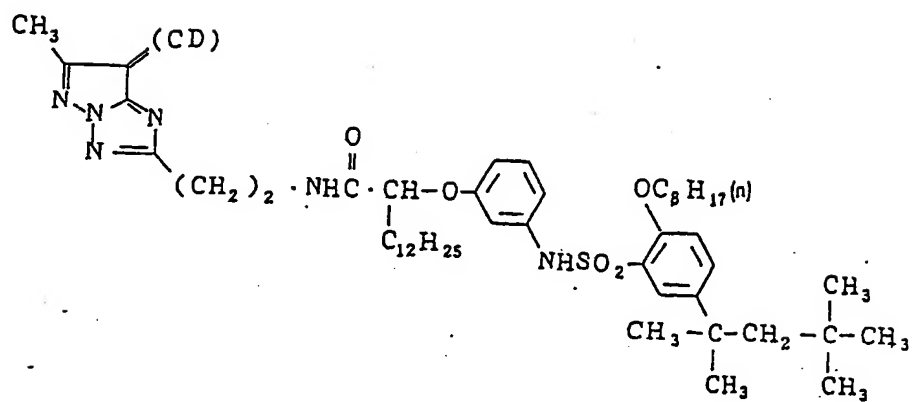
(2)-3



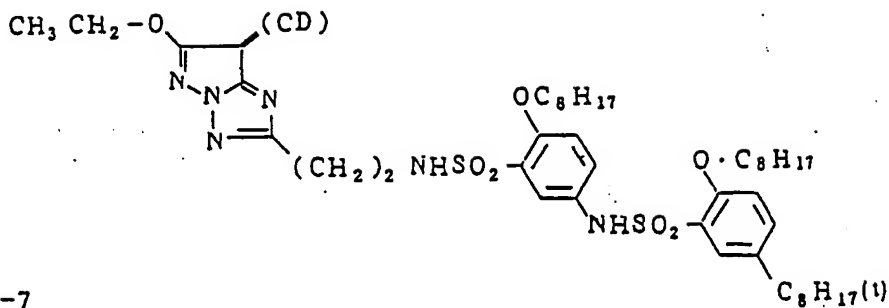
(2)-4



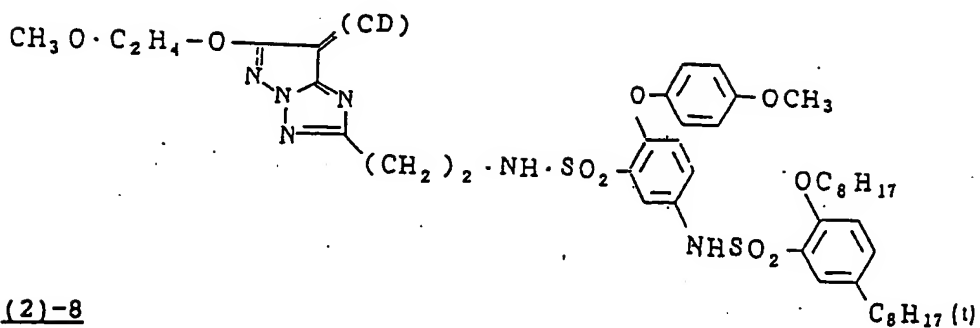
(2)-5



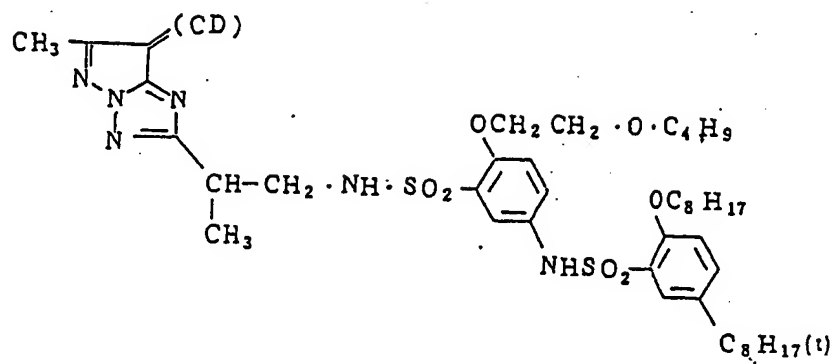
(2)-6



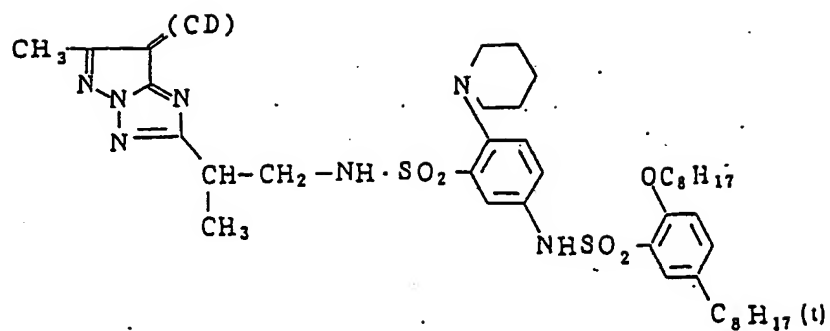
(2)-7



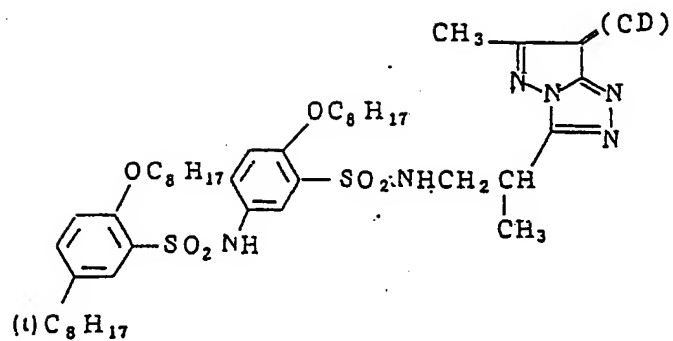
(2)-8



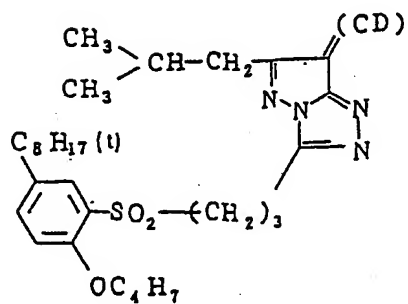
(2)-9



(2)-10

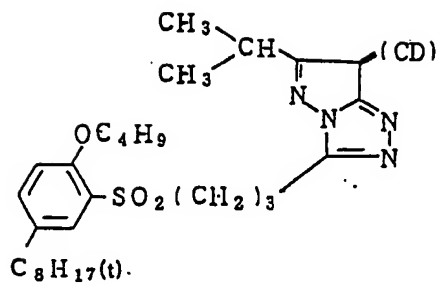


(2)-11

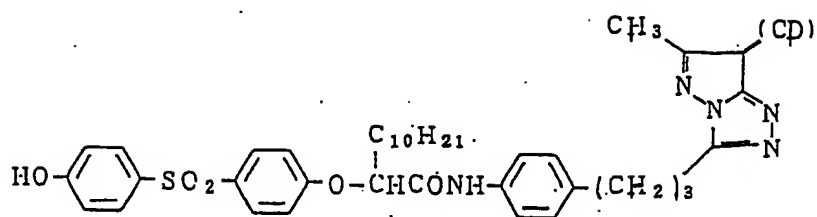




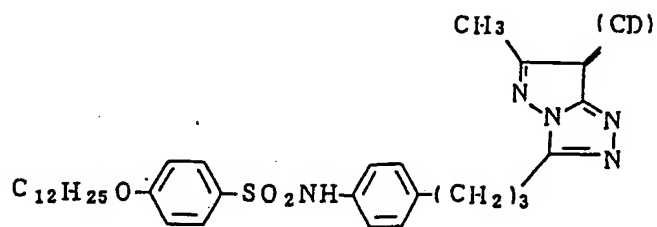
(2)-12



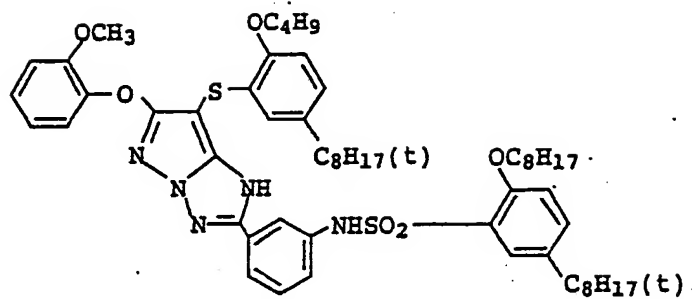
(2)-13



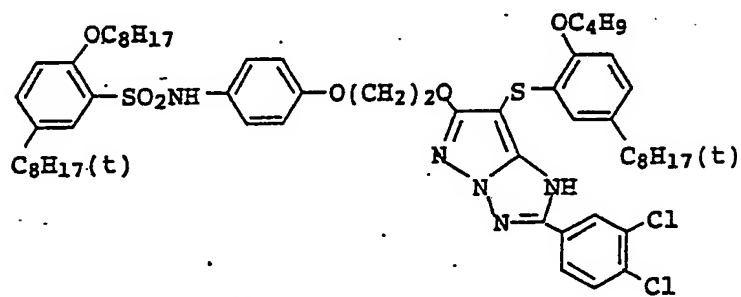
(2)-14



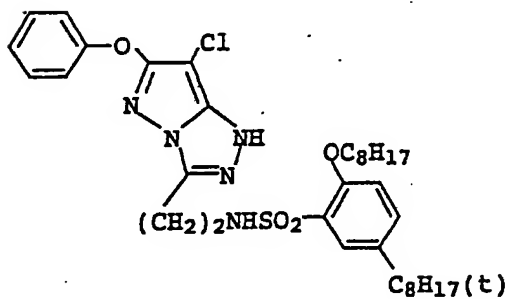
(2)-15



(2)-16

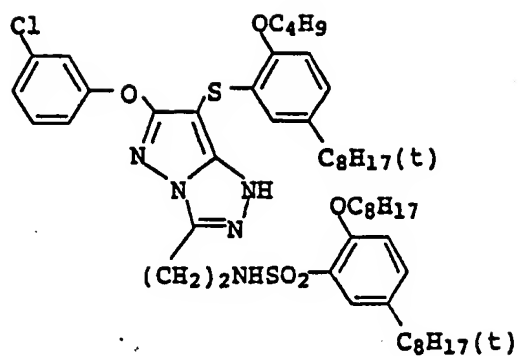


(2)-17

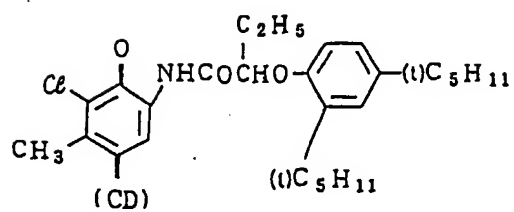


0 270 078

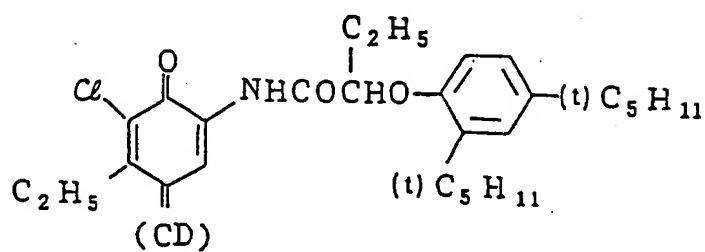
(2)-18



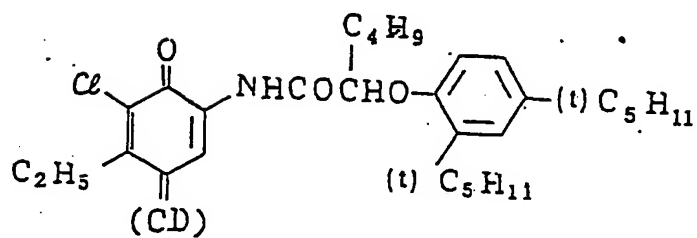
(4)-1



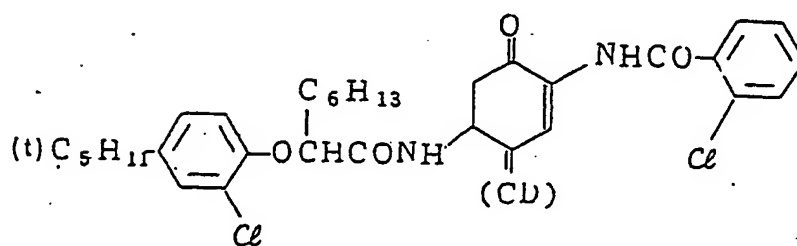
(4)-2



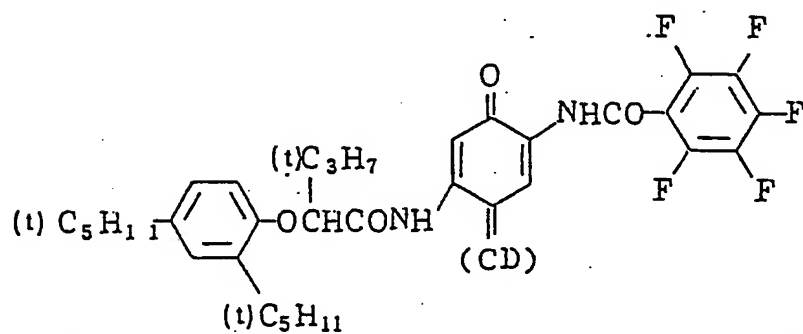
(4)-3



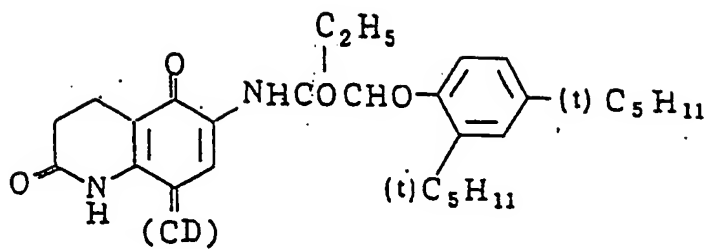
(5)-1



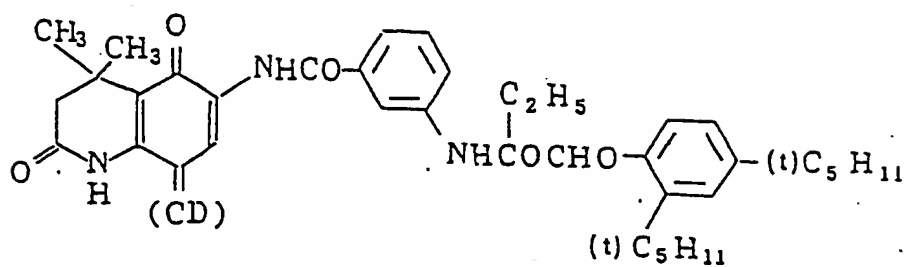
(5)-2



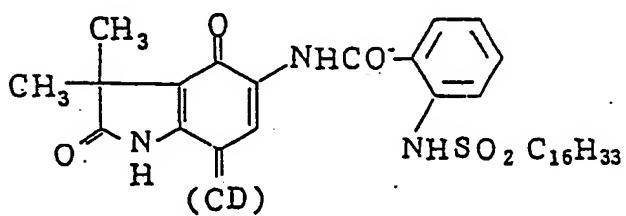
(5)-3



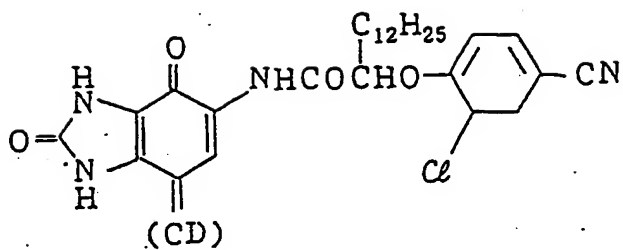
(5)-4



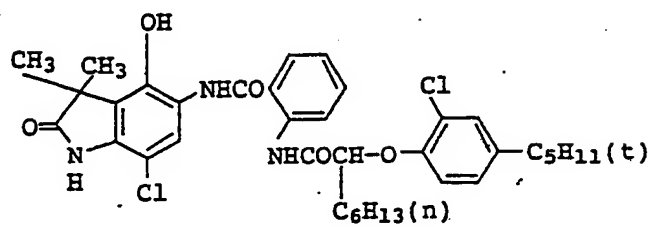
(5)-5



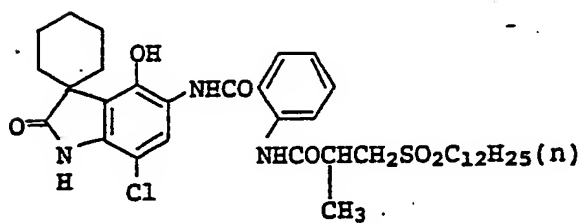
(5)-6



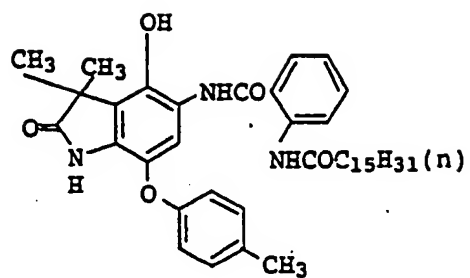
(5)-7



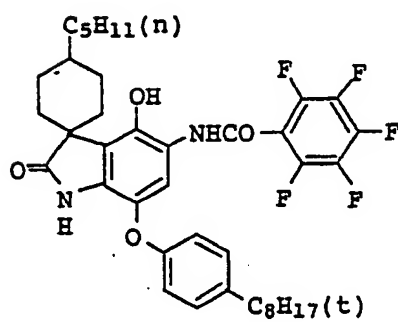
(5)-8



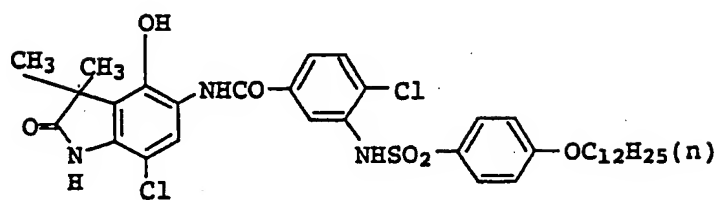
(5)-9



(5)-10



(5)-11

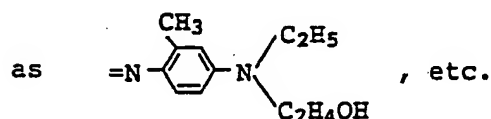


In the above-described formulae, (CD) may represent

$$\text{sent } =\text{N}-\text{C}_6\text{H}_3(\text{CH}_3)-\text{N} \begin{cases} \text{C}_2\text{H}_5 \\ \text{C}_2\text{H}_4\text{NHSO}_2\text{CH}_3 \end{cases}$$

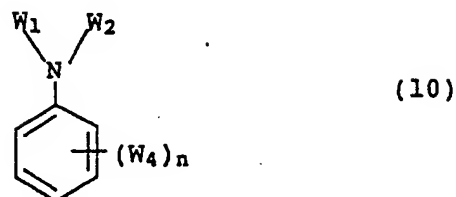
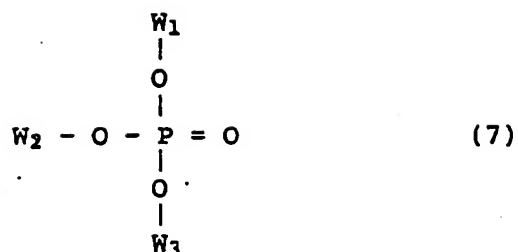
Further, (CD) may represent a

coupling residue of a p-phenylenediamine derivative such



The dyes which form images according to the present invention are preferably used in combination with one or more kinds of organic solvents having a high boiling point of at least 160°C represented by the general formula (7), (8), (9), (10) or (11) as shown below. Details of these organic solvents are described in Japanese Patent Application (OPI) No. 215272/87, pages 138 to 144. Further, it is particularly preferred that the dyes are used in combination with water-insoluble, organic solvent-soluble polymers as described in Japanese Patent Publication No. 30474/73, U.S. Patent 3,619,195 and International Application No. PCT/JP 87/00492 filed July 9, 1987, etc. Moreover, the dyes may be used in combination with loaded polymeric latexes as described in U.S. Patent 4,203,716.





wherein  $W_1$ ,  $W_2$  and  $W_3$  each represents a substituted or unsubstituted alkyl group, a substituted or unsubstituted cycloalkyl group, a substituted or unsubstituted alkenyl group, a substituted or unsubstituted aryl group or a substituted or unsubstituted heterocyclic group;  $W_4$  represents  $W_1$ ,  $-O-W_1$  or  $-S-W_1$ ;  $n$  represents an integer from 1 to 5, when  $n$  is two or more, two or more  $W_4$ 's may be the same or different; and  $W_1$  and  $W_2$  in the general

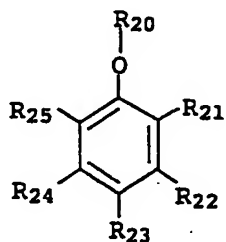
formula (11) may be connected with each other to form a condensed ring.

Preferred specific examples of water-insoluble, organic solvent-soluble polymers include polyvinyl acetate, polyvinyl propionate, and polymethyl methacrylate, but the present invention should not be construed as being limited thereto.

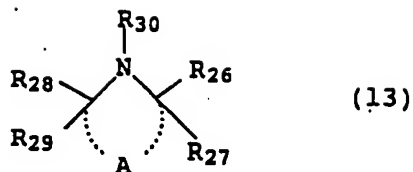
Further, the specific examples of polymers (P-4) to (P-158) as described in International Application No. PCT/JP 87/00492, pages 22 to 30, and the specific examples of polymers 1 to 35 as described in Japanese Patent Publication No. 30494/73, pages 4 to 5 are also preferred.

These polymers may be employed together with the above described organic solvent having a high boiling point of at least 160°C.

Furthermore, it is preferred that the dyes according to the present invention are used in combination with color fading preventing agents or antioxidizing agents represented by the general formula (12) or (13) shown below. Of these compounds, those which are soluble in organic solvents are preferred.



(12)



wherein  $R_{20}$  represents a hydrogen atom, an aliphatic group, an aromatic group, a heterocyclic group or a hydrolyzable protective group;  $R_{21}$ ,  $R_{22}$ ,  $R_{23}$ ,  $R_{24}$  and  $R_{25}$ , which may be the same or different, each represents a hydrogen atom or a substituent;  $R_{30}$  represents a hydrogen atom, an aliphatic group, an acyl group, a sulfonyl group, a sulfinyl group, an oxy radical group or a hydroxy group; A represents a non-metallic atomic group necessary to form a 5-membered, 6-membered or 7-membered ring; and  $R_{26}$ ,  $R_{27}$ ,  $R_{28}$  and  $R_{29}$ , which may be the same or different, each represents a hydrogen atom or an alkyl group.

Specific examples of substituents represented by  $R_{21}$  or  $R_{25}$  include a hydrogen atom and an alkyl group, and preferred examples of the alkyl group include a straight chain or branched chain alkyl group having from 1 to 8 carbon atoms, particularly include a methyl group, an n-butyl group, a t-butyl group, a t-pentyl group and a n-octyl group. Specific examples of substituents represented by  $R_{22}$ ,  $R_{23}$  or  $R_{24}$  include a hydrogen atom, an alkyl group,  $-NHR_{31}$ , an alkoxy group,  $-COO-R_{32}$ , etc., and  $R_{31}$  represents a nitrogen-containing heterocyclic group and  $R_{32}$  represents an alkyl group or an aryl group. The

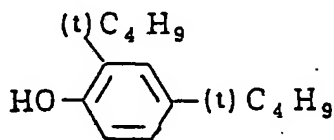
above-mentioned alkyl, alkoxy or aryl group means a substituted or unsubstituted alkyl, alkoxy or aryl group.

Of the substituents represented in the general formula (12),  $R_{20}$  and  $R_{21}$  or two of  $R_{21}$ ,  $R_{22}$ ,  $R_{23}$ ,  $R_{24}$  and  $R_{25}$  which are present in the ortho-positions each other may be connected with each other to form a 5-membered, 6-membered or 7-membered ring.

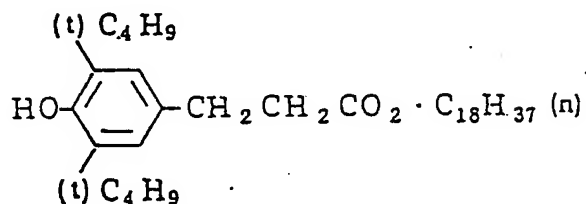
Of the substituents represented in the general formula (13),  $R_{26}$  and  $R_{27}$ ,  $R_{28}$  and  $R_{29}$  or  $R_{30}$  and  $R_{26}$  may be connected with each other to form a 5-membered, 6-membered or 7-membered ring.

Specific examples of the compounds represented by the general formula (12) or (13) are set forth below, but the present invention should not be construed as being limited thereto.

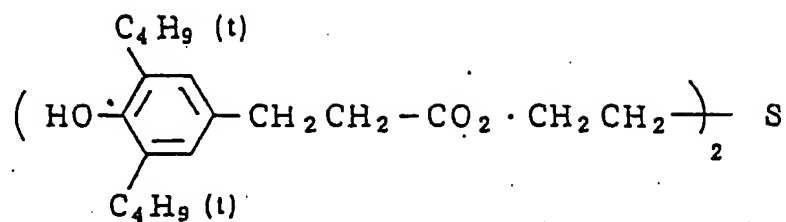
(12)-1



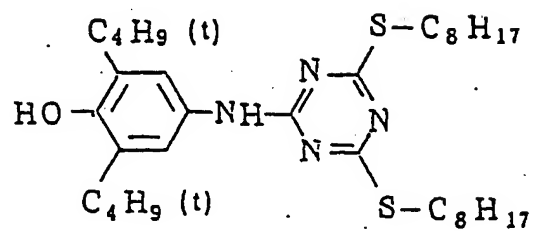
(12)-2



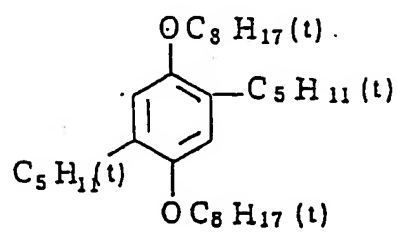
(12)-3



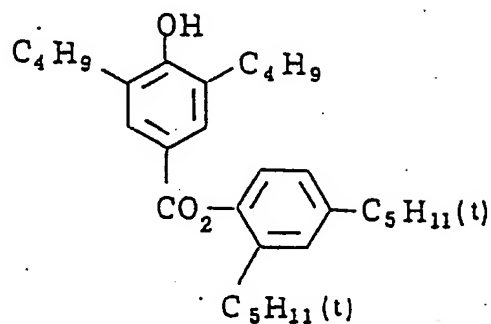
(12)-4



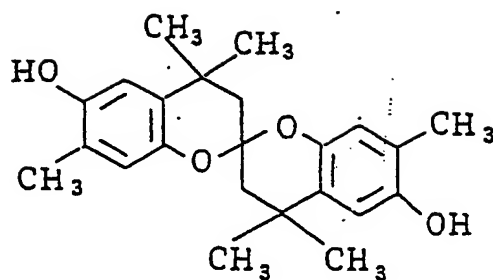
(12)-5



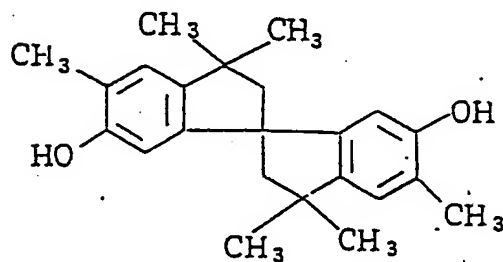
(12)-6



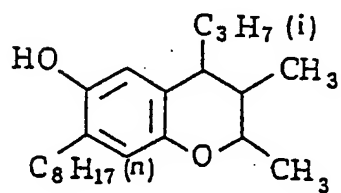
(12)-7



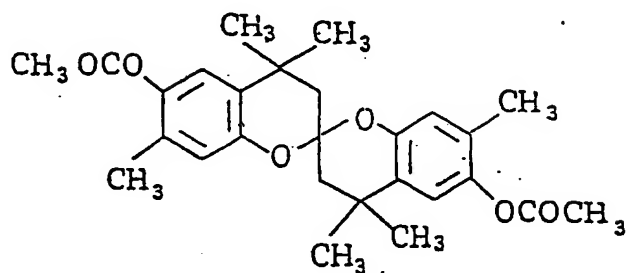
(12)-8



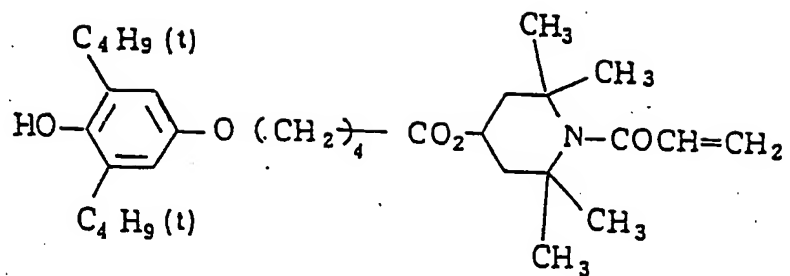
(12)-9



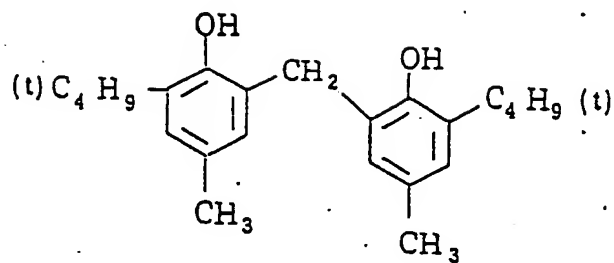
(12)-10



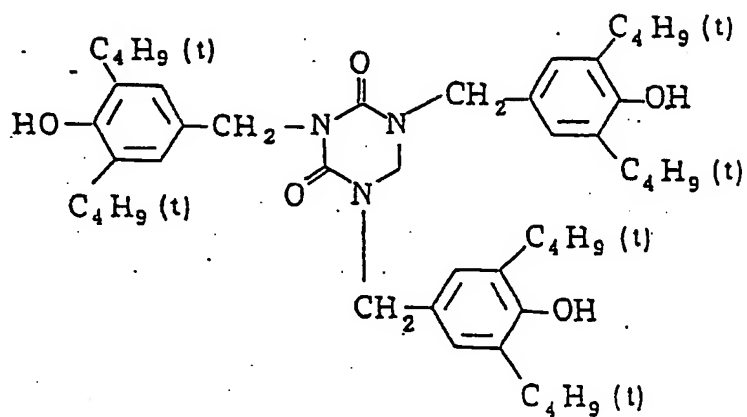
(12)-11

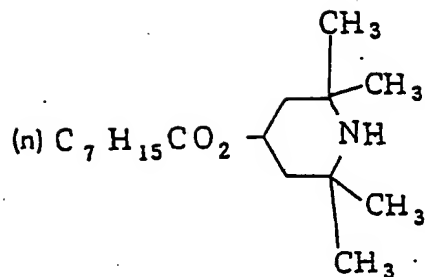
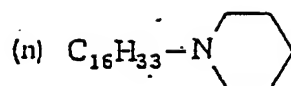
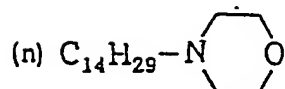


(12)-12



(12)-13



(13)-1(13)-2(13)-3

The color print according to a preferred embodiment of the present invention can be obtained by subjecting, after imagewise exposure, color printing paper which comprises a thin reflective support having thereon a yellow color forming layer containing a blue-sensitive silver halide emulsion and a yellow color forming coupler, a magenta color forming layer containing a green-sensitive



silver halide emulsion and a magenta color forming coupler, and a cyan color forming layer containing a red-sensitive silver halide emulsion and a cyan color forming coupler, and optionally further an antihalation layer, an intermediate layer, a yellow filter layer, a protective layer, etc., if appropriate for the desired photographic material to color development processing.

The silver halide emulsion which is used in the present invention is usually prepared by mixing an aqueous solution of a water-soluble silver salt (for example, silver nitrate) with an aqueous solution of a water-soluble halide (for example, potassium bromide, sodium chloride, potassium iodide or a mixture thereof) in the presence of an aqueous solution of a water-soluble polymer (for example, gelatin, etc.). As the silver halide thus-prepared, in addition to silver chloride and silver bromide, a mixed silver halide, for example, silver chlorobromide, silver chloriodobromide, silver iodobromide, etc. are representative examples. The silver halide which is preferably employed in the present invention is silver chloriodobromide, silver iodochloride or silver iodobromide, each containing 3 mol% or less silver iodide.

Silver halide grains may have different layers in the inner portion and the surface portion, multi-phase structures containing junctions, or may be uniform

throughout the grains. Further, a mixture of these silver halide grains having different structures may be employed. For instance, with respect to silver chlorobromide grains having different phases, those having nuclei or a single layer or plural layers which are rich in silver bromide as compared with the mean halogen composition in their inner portion, or those having nuclei or a single layer or plural layers which are rich in silver chloride as compared with the mean halogen composition in their inner portion may be employed. Therefore, surface layers of the grains are rich in silver bromide as compared with the mean halogen composition or contrary to this, surface layers are rich in silver chloride.

Average grain size of silver halide grains (the grain size being defined as grain diameter if the grain has a spherical or a nearly spherical form and as a length of the edge if the grain has a cubic form, and being averaged based on projected areas of the grains) is preferably from  $0.1\ \mu$  to  $2\ \mu$ , and particularly from  $0.15\ \mu$  to  $1\ \mu$ . Grain size distribution may be either narrow or broad.

A so-called monodispersed silver halide emulsion having narrow grain size distribution which comprises at least 90%, particularly at least 95% by number or by weight of the total silver halide grains having a size within the range of the average grain size  $\pm 40\%$  is

preferably employed in the present invention. Further, in order to achieve the desired gradation of the light-sensitive material, two or more monodispersed silver halide emulsions which have different grain sizes from each other can be mixed in one emulsion layer or can be coated in the form of superimposed layers which have substantially the same spectral sensitivity. Moreover, two or more polydispersed silver halide emulsions or combinations of a monodispersed emulsion and a polydispersed emulsion may be employed in a mixture or in the form of superimposed layers.

Silver halide grains which can be used in the present invention may have a regular crystal structure, for example, a cubic, octahedral, dodecahedral or tetradecahedral structure, etc., an irregular crystal structure, for example, a spherical structure, etc., or a composite structure thereof. Further, tabular silver halide grains can be used. Particularly, a silver halide emulsion wherein tabular silver halide grains having a ratio of diameter/thickness of not less than 5, preferably not less than 8 account for at least 50% of the total silver halide grains present calculated based on projected area of the silver halide grains can be employed. In addition, mixtures of silver halide grains having different crystal structures may be used. These silver halide emulsions may be those of surface latent image type

in which latent images are formed mainly on the surface thereof, or those of internal latent image type in which latent images are formed mainly in the interior thereof.

Dyes are employed in the present invention for various purposes, for example, as filter dyes, for irradiation prevention, for antihalation, etc. Examples of such dyes which are preferably used are oxonol dyes, hemioxonol dyes, styryl dyes, merocyanine dyes, anthraquinone dyes and azo dyes. Further, cyanine dyes, azomethine dyes, triarylmethane dyes and phthalocyanine dyes are also useful. Oil-soluble dyes may be added to a hydrophilic colloid layer by emulsification using an oil droplet-in-water dispersing method.

In the color photographic light-sensitive material of the present invention, inorganic or organic hardening agents are employed in order to harden the hydrophilic colloid layers applied on the support. For example, active halogen compounds (for example, 2,4-dichloro-6-hydroxy-1,3,5-triazine, etc.) and active vinyl compounds (for example, 1,3-bisvinylsulfonyl-2-propanol, 1,2-bisvinylsulfonylacetamidoethane, a vinyl type polymer having a vinylsulfonyl group in its side chain, etc.) are preferred since they rapidly act on a hydrophilic colloid such as gelatin to harden and provide stable photographic properties. Also N-carbamoylpyridinium salts and halo-

amidinium salts are excellent in view of their high hardening speed.

A color developing solution used for development processing of the color photographic light-sensitive material of the present invention to obtain a color print is preferably an alkaline aqueous solution containing an aromatic primary amine color developing agent as a main component. As a color developing agent, while an aminophenol type compound is useful, a p-phenylenediamine type compound is preferably used. Typical examples of the p-phenylenediamine type compounds include 3-methyl-4-amino-N,N-diethylaniline, 3-methyl-4-amino-N-ethyl-N- $\beta$ -hydroxyethylaniline, 3-methyl-4-amino-N-ethyl-N- $\beta$ -methanesulfonamidoethylaniline, 3-methyl-4-amino-N-ethyl-N- $\beta$ -methoxyethylaniline, or a sulfate, hydrochloride or p-toluenesulfonate thereof, etc. These diamines are preferably employed in the form of salts since the salts are generally more stable than their free forms.

The color developing solution generally contains pH buffering agents such as carbonates, borates or phosphates of alkali metals, etc., and development inhibitors or antifogging agents such as bromides, iodides, benzimidazoles, benzothiazoles or mercapto compounds, etc. In addition, if desired, the color developing solution may also contain, for example, preservatives such as hydroxylamine, derivatives thereof

(for example, N,N-dialkyl substituted derivatives, etc.), sulfites, etc.; organic solvents such as triethanolamine, derivatives thereof, diethylene glycol, etc.; development accelerators such as benzylalcohol, polyethyleneglycol, quaternary ammonium salts, amines, etc.; competing couplers; nucleating agents such as sodium borohydride, etc.; auxiliary developing agents such as 1-phenyl-3-pyrazolidone, etc.; viscosity imparting agents; various chelating agents as represented by aminopolycarboxylic acids, aminopolyphosphonic acids, alkylphosphonic acids and phosphonocarboxylic acids, etc.; and antioxidants as described in West German Patent Application (OLS) No. 2,622,950.

In the case of development processing for reversal color photographic light-sensitive materials, color development is usually conducted after black-and-white development.

After color development, the photographic emulsion layer is usually subjected to a bleach processing. The bleach processing can be carried out simultaneously with or separately from a fix processing. Further, in order to perform a rapid processing, a processing method in which a bleach-fix processing is conducted after a bleach processing can be employed. As bleaching agents, iron (III) salts of ethylenediaminetetraacetic acid, iron (III) salts of diethylenetriaminepentaacetic acid and per-

sulfates are preferred in view of rapid processing and less environmental pollution. Further, ethylenediamine-tetraacetic acid iron (III) complex salts are particularly useful both in an independent bleaching solution and in a mono-bath bleach-fixing solution. Further, thiosulfates are ordinarily employed as fixing agents. In the bleach-fixing solution or the fixing solution, sulfites, bisulfites, carbonylbisulfite adducts, etc. are preferably employed as preservatives.

After the bleach-fix processing or fix processing, water wash processing and/or stabilization processing are usually conducted. In the water washing step or stabilizing step, various known compounds may be employed for the purpose of preventing precipitation or saving water, etc. For example, a water softener such as an inorganic phosphoric acid, an aminopolycarboxylic acid, an organic aminopolyphosphonic acid, or an organic phosphoric acid, etc. for the purpose of preventing the formation of precipitation; a sterilizer or antimold for the purpose of preventing the propagation of various bacteria, algae and molds; a metal salt such as a magnesium salt, an aluminum salt, a bismuth salt, etc.; or a surface active agent for the purpose of reducing drying load or preventing drying marks; various hardening agents; etc. may be added, if desired. Further, the compounds as described in L.E. West, Photo. Sci. Enq., Vol. 6, pages

344 to 359 (1965) may be added. Particularly, the addition of chelating agents and antimolds is effective.

Further, the color photographic light-sensitive material according to the present invention may contain, if appropriate, various 1-phenyl-3-pyrazolidones for the purpose of accelerating color development. Typical examples of the compounds include those as described in Japanese Patent Application (OPI) Nos. 64339/81, 144547/82, 211147/82, 50532/83, 50536/83, 50533/83, 50534/83, 50535/83 and 115438/83, etc.

In the present invention, various kinds of processing described above can be conducted in a temperature range of from 10°C to 50°C. Although a standard temperature is from 33°C to 38°C, it is possible to carry out the processing at higher temperatures in order to accelerate the processing whereby the processing time is shortened, or on the other hand, at lower temperatures in order to achieve improvement in image quality and to maintain stability of the processing solutions.

Further, for the purpose of reducing the amount of silver employed in the color photographic light-sensitive material, the photographic processing may be conducted utilizing color intensification using cobalt or hydrogen peroxide as described in West German Patent Application (OLS) No. 2,226,770 or U.S. Patent 3,674,499.



Moreover, in the case of continuous processing, the variation of composition in each processing solution can be prevented by using a replenisher for each processing solution, whereby a constant finish can be achieved. The amount of replenisher can be reduced to one half or less of the standard amount of replenishment for the purpose of reducing cost.

Direct positive color prints can be obtained with respect to the color photographic light-sensitive materials by using an internal latent image type emulsion which was not previously fogged as a silver halide emulsion, and performing a fogging treatment after imagewise exposure but before or during a color development step.

As the fogging treatment, a method conducting fogging exposure or a method using a nucleating agent (a chemical fogging method) are effective. More specifically, a light fogging method and a chemical fogging method (a method using a nucleating agent together with a nucleating accelerator) as described, for example, in U.S. Application Serial No. 60,790 filed June 12, 1987, pages 55 to 88, or European Patent Application No. 87 108489.3 filed June 12, 1987, pages 55 to 88 (corresponding to Japanese Patent Application No. 136949/86) can be utilized.

The color photographic prints obtained by development processing of the color photographic light-

sensitive materials according to the present invention have advantageously not only good fastness to light, humidity and heat but also excellent sharpness of color images.

Further, since they have good smoothness of emulsion layer, irregularity of color image density is remarkably reduced.

Moreover, the support composed of a vinyl chloride resin used in the present invention is excellent in flexibility and strength and its degree of elasticity depending on change in humidity is small and can be ignored in comparison with other photographic supports.

Furthermore, it is easy to emboss a card after printing and thus the color photographic light-sensitive materials and the color photographic prints according to the present invention are particularly suitable for employing as ID cards, cashing cards and telephone cards, etc.

The present invention is explained in greater detail with reference to the following examples, but the present invention should not be construed as being limited thereto.

#### EXAMPLE 1

On a support which was composed of a hard vinyl chloride resin (a copolymer containing at least 50 mol% of vinyl chloride monomer component, with the remainder

thereof being vinylidene chloride and methyl methacrylate, and further containing 12 parts by weight of  $\text{TiO}_2$  per 100 parts of total weight of the copolymer) and had a thickness of 150  $\mu\text{m}$  and an average reflectance in the visible range of 85% or more, provided with subbing treatment, the first layer to the seventh layer described below were coated to prepare a color photographic light-sensitive material which was designated Sample 101. The support used was in conformity with a standard of JIS-K-6734-Class C, No. 1, as described in JIS published by Japanese Standards Association.

Coated amounts shown below are  $\text{g/m}^2$ , and coated amounts of silver halide shown below are measured as silver.

First Layer: Blue-Sensitive Layer

Silver chlorobromide emulsion (silver bromide: 80 mol%)	0.30 (as silver)
Yellow coupler (*1)	0.70
Solvent (TNP)	0.15
Gelatin	1.20

Second Layer: Intermediate Layer

Gelatin	0.90
Di-tert-octylhydroquinone	0.05
Solvent (DBP)	0.10

Third Layer: Green-Sensitive Layer

Silver chlorobromide emulsion (silver bromide: 70 mol%)	0.45 (as silver)
--	---------------------

Magenta Coupler (*2)	0.35
Solvent (TOP)	0.44
Color fading preventing agent (*3/*4)	0.05/0.10
Gelatin	1.00

Fourth Layer: Ultraviolet Ray Absorbing Intermediate Layer

Ultraviolet ray absorbing agent (*5/*6/*7)	0.06/0.25/0.25
Solvent (TNP)	0.20
Gelatin	1.50

Fifth Layer: Red-Sensitive Layer

Silver chlorobromide emulsion (silver bromide: 50 mol%)	0.20 (as silver)
Cyan Coupler (*8/*9)	0.2/0.2
Solvent (TNP/DBP)	0.10/0.20
Gelatin	0.9

Sixth Layer: Ultraviolet Ray Absorbing Intermediate Layer

Ultraviolet ray absorbing agent (*5/*6/*7)	0.06/0.25/0.25
Solvent (DBP)	0.20
Gelatin	1.5

Seventh Layer: Protective Layer

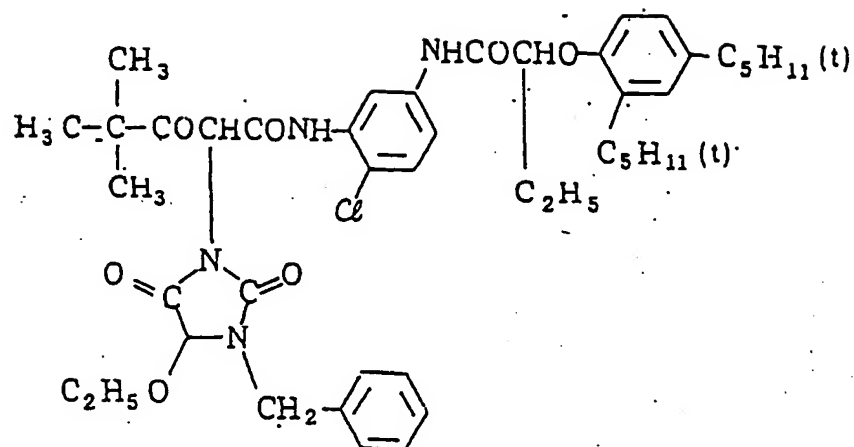
Gelatin	1.5
---------	-----

DBP: Dibutyl phthalate

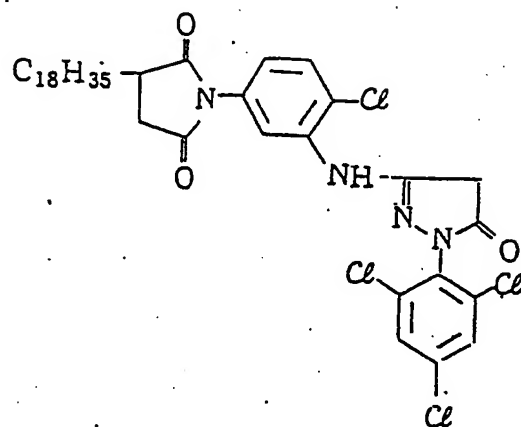
TOP: Tri(n-octylphosphate)

TNP: Tri(n-nonylphosphate)

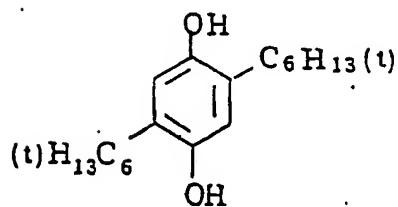
( \* / )



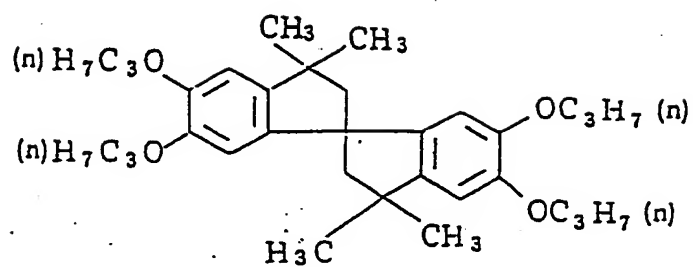
( \* 2 )



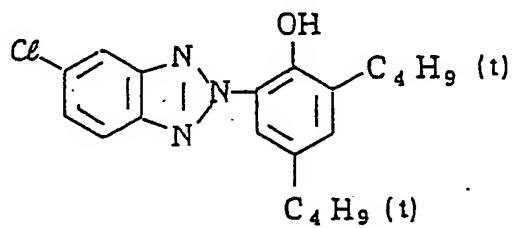
( \* 3 )



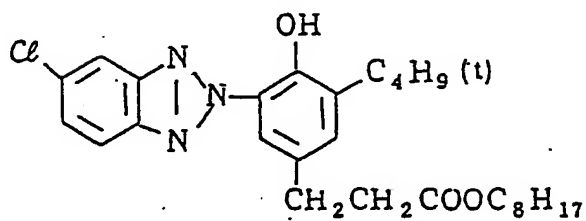
( \* 4 )



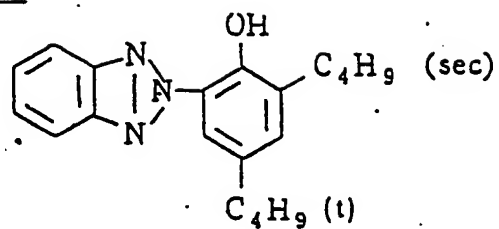
( \* 5 )



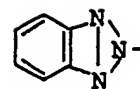
( \* 6 )



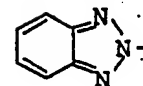
( \* 7 )



Note) In the formula, the skeleton

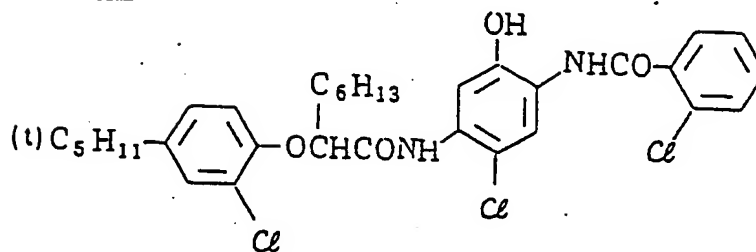


may change into a structure

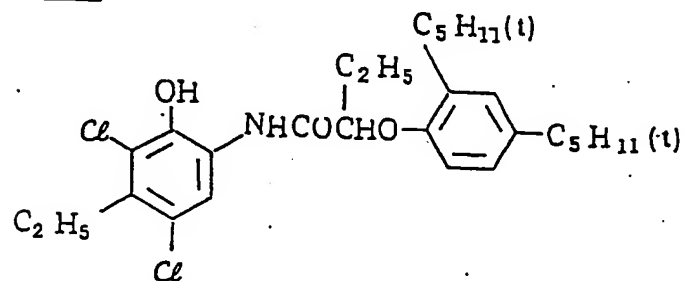


due to a resonance effect.

( \* 8 )



( \* 9 )



The following dyes were used as spectral sensitizing dyes in the emulsion layers, respectively.

Blue-sensitive Emulsion Layer:

4-(5-chloro-2-[5-chloro-3-(4-sulfonatobutyl)benzothiazolin-2-ylidenemethyl]-3-benzothiazolino)-butanesulfonatotriethylammonium salt ( $2 \times 10^{-4}$  mol per mol of silver halide)

Green-Sensitive Emulsion Layer:

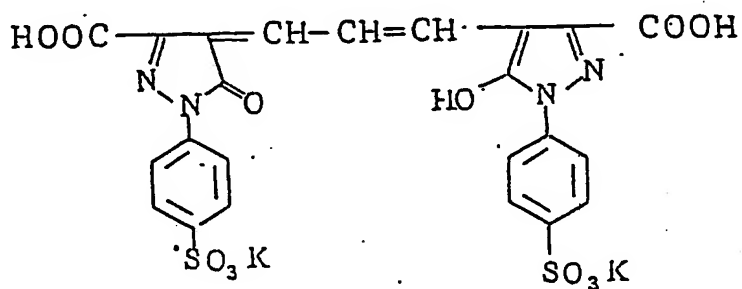
3,3'-Di-( $\gamma$ -sulfopropyl)-5,5'-diphenyl-9-ethoxycarbocyanine sodium salt ( $2.5 \times 10^{-4}$  mol per mol of silver halide)

Red-Sensitive Emulsion Layer:

3,3'-Di-( $\gamma$ -sulfopropyl)-9-methylthiacarbocyanine sodium salt ( $2.5 \times 10^{-4}$  mol per mol of silver halide)

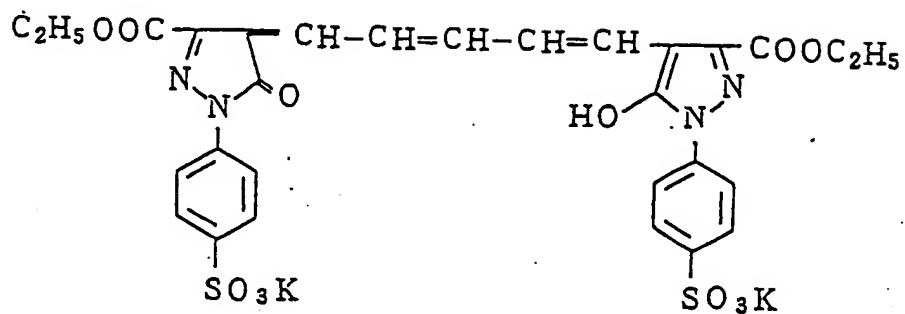
The following dyes were employed as irradiation preventing dyes in the emulsion layers, respectively.

Green-sensitive Emulsion Layer:





## Red-sensitive Emulsion Layer:

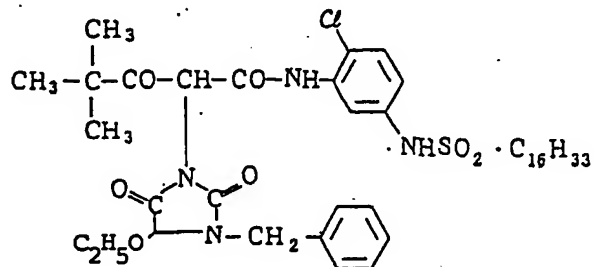


Samples 102 and A' were prepared in the same manner as described for Sample 101 except for changing couplers as shown in Table 1 below.

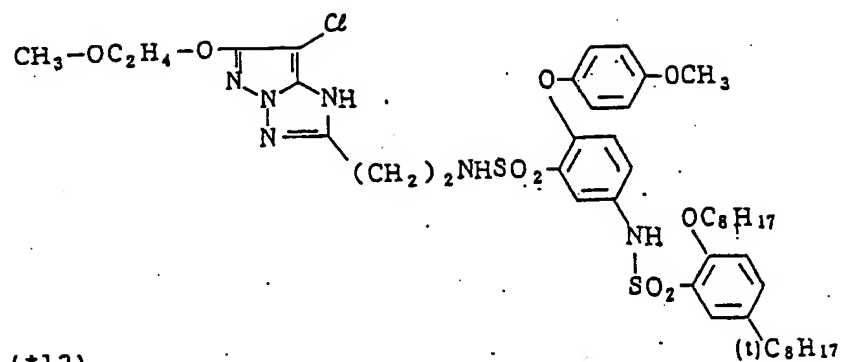
TABLE 1

Layer	Sample 101	Sample 102	Sample A'
First Layer	Yellow coupler (*1)	Coupler forming Dye (1)-4 (*10)	*A-1
Third Layer	Magenta coupler (*2)	Coupler forming Dye (2)-7 (*11)	*A-2
Fifth Layer	Cyan coupler (*8/*9)	Cyan coupler (*8)/Coupler forming Dye (5)-5 (*12)	*A-3

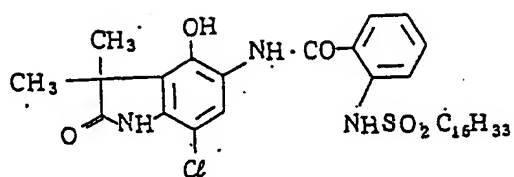
(\*10)



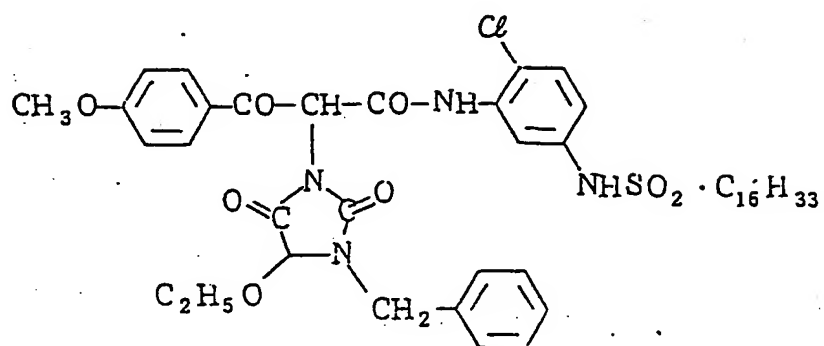
(\*11)



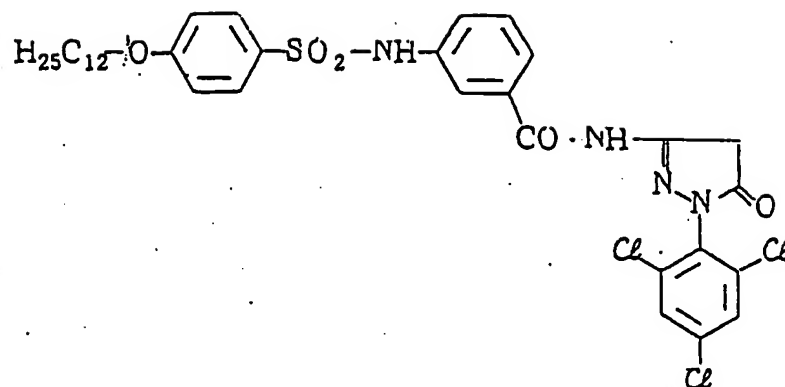
(\*12)



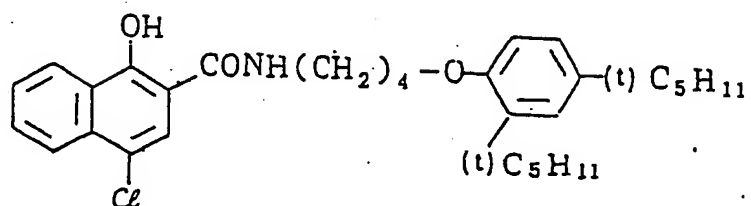
(\*A-1)



(\*A-2)



(\*A-3)



These samples were stepwise exposed and then subjected to development processing according to the processing steps as shown below.

<u>Processing Step</u>	<u>Temperature</u>	<u>Time</u>
Development	33°C	3 min. 30 sec.
Bleach-fixing	33°C	1 min. 30 sec.
Washing with Water	28 to 35°C	3 min.

The composition of each processing solution used in the above-described processing steps is as follows:

### Developing Solution

Trisodium nitrilotriacetate                      2.0 g

Benzyl alcohol	15 ml
Diethylene glycol	10 ml
Sodium sulfite	2.0 g
Potassium bromide	0.5 g
Hydroxylamine sulfate	3.0 g
4-Amino-3-methyl-N-ethyl-N- $[\beta$ -(methanesulfonamido)ethyl]-p-phenylenediamine sulfate	5.0 g
Sodium carbonate (monohydrate)	30 g
Water to make	1 liter
	(pH: 10.1)

Bleach-Fixing Solution

Ammonium thiosulfate (54 wt%)	150 ml
Sodium sulfite	15 g
Ammonium iron (III) ethylene-diaminetetraacetate	55 g
Disodium ethylenediaminetetraacetate	4 g
Water to make	1 liter
	(pH: 6.9)

With Samples 101, 102 and A' thus-processed sharpness was determined. Sharpness is a value to indicate clearness of outlines of images and ability to duplicate fine images. The value known as CTF was used herein. CTF means a degree of decrease in amplitude against a spatial frequency as a rectangular wave. Sharpness at 15 lines/mm of spatial frequency thus-

measured are shown in Table 2 below. The larger value indicates the better sharpness.

TABLE 2

<u>Sharpness</u>	<u>Sample 101</u>	<u>Sample 102</u>	<u>Sample A'*</u>
B	25.4	27.2	22.4
G	33.0	35.6	29.3
R	34.9	37.1	30.7

\* Comparative Sample

Irregularity of image density was not observed in both Samples 101 and 102.

EXAMPLE 2

Silver Halide Emulsion (7) for a blue-sensitive silver halide emulsion layer was prepared in the following manner.

Solution 8

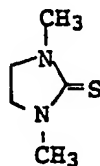
H <sub>2</sub> O	1,000 ml
NaCl	5.8 g
Gelatin	25 g

Solution 9

Sulfuric acid (1N)	20 ml
--------------------	-------

Solution 10

A silver halide solvent (1%) of the formula:



Solution 11

KBr	0.18 g
NaCl	8.51 g
H <sub>2</sub> O to make	130 ml

Solution 12

AgNO <sub>3</sub>	25 g
H <sub>2</sub> O to make	130 ml

Solution 13

Pb(CH <sub>3</sub> COO) <sub>2</sub> ·3H <sub>2</sub> O (0.1%)	28 ml
--	-------

Solution 14

KBr	0.70 g
NaCl	34.05 g
H <sub>2</sub> O to make	285 ml

Solution 15

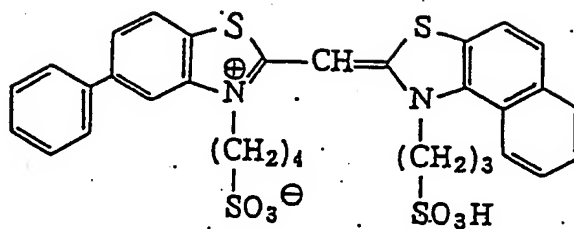
AgNO <sub>3</sub>	100 g
H <sub>2</sub> O to make	285 ml

Solution 8 was heated at 60°C, Solution 9 and Solution 10 were added thereto and then Solution 11 and Solution 12 were added simultaneously over a period of 60 minutes thereto. One minute after the completion of the addition of Solution 11 and Solution 12, Solution 13 was added and then after 9 minutes Solution 14 and Solution 15 were added simultaneously over a period of 25 minutes. After 5 minutes, the temperature was dropped and the mixture was desalted. Water and gelatin for dispersion were added thereto and pH was adjusted to 6.0 whereby a

mono-dispersed cubic silver chlorobromide emulsion (having an average grain size of 1.00  $\mu\text{m}$ , a coefficient of variation of 0.11 and a silver bromide content of 1 mol%) was obtained. The emulsion was subjected to optimum chemical sensitization using triethyl thiourea and chloroauric acid. Thereafter, Spectral Sensitizer (S-1) shown below was added in an amount of  $5 \times 10^{-4}$  mol per mol of silver halide.

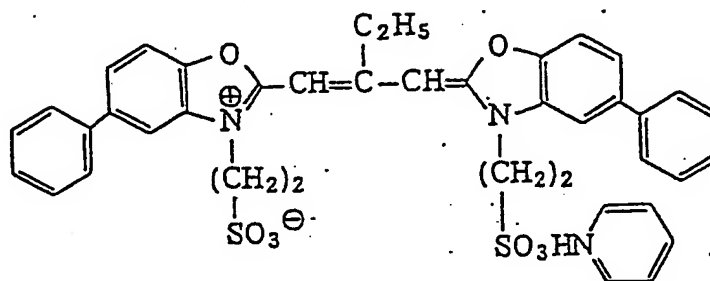
Silver Halide Emulsion (8) for a green-sensitive silver halide emulsion layer and Silver Halide Emulsion (9) for a red-sensitive silver halide emulsion layer were prepared in the same manner as described above except changing amounts of chemicals used in Solution 8 and Solution 10, kinds and amounts of spectral sensitizers, and temperatures and times for addition. Spectral Sensitizer (S-2) shown below was used for Silver Halide Emulsion (8) and Spectral Sensitizer (S-3) shown below was used for Silver Halide Emulsion (9).

Spectral Sensitizer (S-1):

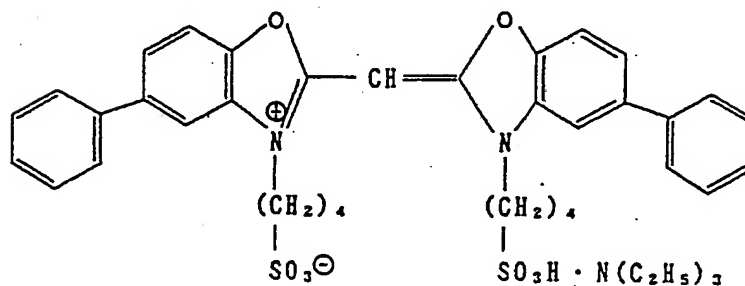


$(5 \times 10^{-4}$  mol per mol of silver halide)

Spectral Sensitizer (S-2):



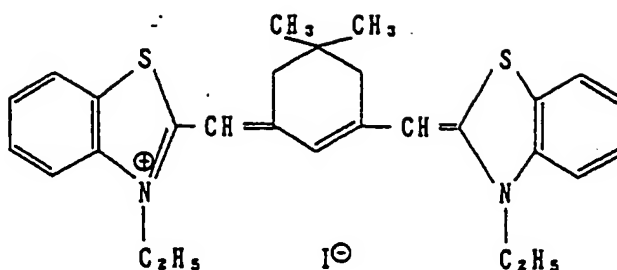
$(4 \times 10^{-4}$  mol per mol of silver halide)



$(7.0 \times 10^{-5}$  mol per mol of silver halide)

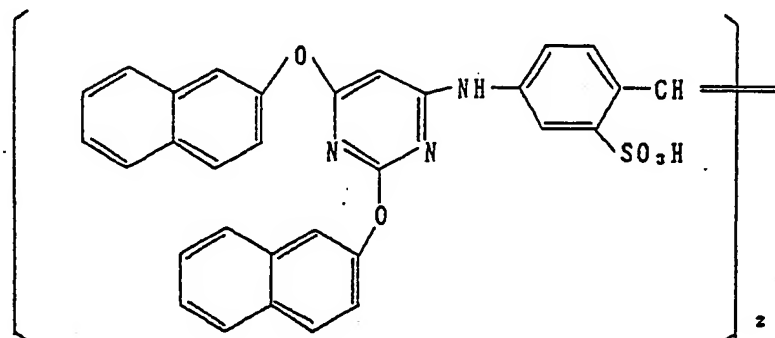


## Spectral Sensitizer (S-3):



( $0.9 \times 10^{-4}$  mol per mol of silver halide)

Further, to the red-sensitive silver halide emulsion layer, the compound described below was added in an amount of  $2.6 \times 10^{-3}$  mol per mol of silver halide.



Moreover, 1-(5-methylureidophenyl)-5-mercaptotetrazole was added to the blue-sensitive emulsion layer, green-sensitive emulsion layer and red-sensitive emulsion layer in the amounts of  $8.5 \times 10^{-5}$  mol,  $7.7 \times 10^{-4}$  mol and  $2.5 \times 10^{-4}$  mol per mol of silver halide present in the layer, respectively.

Average grain sizes, coefficients of variation and halide compositions of Silver Halide Emulsions (7) to (9) are shown in Table 3 below.

TABLE 3

<u>Emulsion</u>	<u>Average Grain Size</u> ( $\mu\text{m}$ )	<u>Coefficient of* Variation (S/<math>\bar{d}</math>)</u>	<u>Halide Composition</u>	
			<u>Br</u> (%)	<u>Cl</u> (%)
(7)	1.00	0.11	1.0	99.0
(8)	0.44	0.10	0.4	99.6
(9)	0.53	0.09	1.0	99.0

\* S means a standard deviation in statistics and is represented by

$$S = \sqrt{\frac{\sum (r - \bar{r})^2 n_i}{\sum n_i}}$$

and  $\bar{d}$  means an average grain size.

Samples 103 and 104 were prepared in the same manner as described for Samples 101 and 102, respectively, except that the silver halide emulsions used in the first layer, the third layer and the fifth layer were changed to Silver Halide Emulsions (7), (8) and (9), respectively. These samples were stepwise exposed in the same manner as described in Example 1 and then subjected to development processing consisting of color development, bleach-fixing and rinse steps as shown below.

<u>Processing Step</u>	<u>Temperature</u>	<u>Time</u>
Color Development	35°C	45 sec.
Bleach-Fixing	35°C	45 sec.
Rinse	28 to 35°C	1 min. 30 sec.

The composition of each processing solution used in the above-described processing steps are as follows:

Color Developing Solution:

Water	800 ml
Pentasodium diethylene-triaminepentaacetate	1.0 g
Sodium sulfite	0.2 g
N,N-Diethylhydroxylamine	4.2 g
Potassium bromide	0.01 g
Sodium chloride	1.5 g
Triethanolamine	8.0 g
N-Ethyl-N-( $\beta$ -methanesulfonamidoethyl)-3-methyl-4-amino-aniline sulfate	4.5 g
Potassium carbonate	30.0 g
4,4'-Diaminostilbene type brightening agent (Whitex 4 manufactured by Sumitomo Chemical Co., Ltd.)	2.0 g
Water to make	1,000 ml
	pH 10.1

Bleach-Fixing Solution:

Water	700 ml
Ammonium thiosulfate (54% by weight aq. soln.)	150 ml
Sodium sulfite	15 g
NH <sub>4</sub> [Fe(III)(EDTA)]	55 g
EDTA·2Na·2H <sub>2</sub> O	4 g
Glacial acetic acid	8.61 g

Water to make	1,000 ml
	pH 5.4

Rinse Solution:

EDTA·2Na·2H <sub>2</sub> O	0.4 g
Water to make	1,000 ml
	pH 7.0

Sharpness of the samples thus-processed was measured and it was determined that further improvement in sharpness was obtained.

EXAMPLE 3

1) Preparation of Emulsions

Emulsions A to H were prepared as follows.

Emulsion A

An aqueous solution of potassium bromide and an aqueous solution of silver nitrate were simultaneously added to a gelatin aqueous solution under vigorous stirring at 75°C over a period of 40 minutes to obtain a monodispersed silver bromide emulsion containing octahedral grains of 0.4 µm in average grain size. Four mg of sodium thiosulfate and 4 mg of chloroauric acid (4 hydrate) were added to the emulsion per mol of silver, followed by heating at 75°C for 80 minutes to effect chemical sensitization. The thus obtained silver bromide grains were used as cores, and were allowed to further grow in the same precipitating environment as the first step for 40 minutes to finally obtain an octahedral

monodispersed core/shell silver bromide emulsion of 0.6  $\mu$ m in average grain size (coefficient of variation : 14%). After washing with water and desalting of the emulsion, 0.9 mg of sodium thiosulfate was added thereto per mol of silver, followed by heating at 65°C for 60 minutes to effect chemical sensitization. Thus, internal latent image type silver halide emulsion A was obtained.

#### Emulsion B

30 g of gelatin was added to 1 liter of a solution containing 0.5 mol of KBr, 0.2 mol of NaCl and 0.0015 mol of KI and dissolved. To the solution was added 700 ml of a 1 mol/l silver nitrate aqueous solution at 60°C over a period of 20 minutes, followed by effecting physical ripening for 20 minutes. The emulsion was washed with water to remove water-soluble halides, then 20 g of gelatin was added thereto, and thereafter water was added thereto to make the total volume 1,200 ml. Thus, an emulsion of 0.4  $\mu$ m in average grain size was obtained. The emulsion was washed with water and desalted to obtain internal latent image type silver halide emulsion B.

#### Emulsion C

30 g of gelatin was added to 1 liter of a solution containing 0.5 mol of KBr, 0.2 mol of NaCl and 0.0015 mol of KI and dissolved. To the solution was added 700 ml of a 1 mol/l silver nitrate aqueous solution at 60°C over a period of 20 minutes, followed by effecting physical

ripening for 20 minutes. The emulsion was washed with water to remove water-soluble halides, then 20 g of gelatin was added thereto, and thereafter water was added thereto to make the total volume 1,200 ml. Thus, an emulsion of 0.4  $\mu$ m in average grain size was obtained. To 300 ml of the emulsion were added simultaneously 500 ml of a 1 mol/l silver nitrate aqueous solution and 500 ml of a 2 mol/l sodium chloride aqueous solution at 60°C to precipitate silver chloride shells, followed by washing with water. Thus, silver halide emulsion C of 0.7  $\mu$ m in average grain size was obtained.

#### Emulsion D

An aqueous solution of potassium bromide and an aqueous solution of silver nitrate were simultaneously added to a gelatin aqueous solution under vigorous stirring at 75°C over a period of 40 minutes to obtain a monodispersed silver bromide emulsion containing octahedral grains of 0.4  $\mu$ m in average grain size. Four mg of sodium thiosulfate and 4 mg of chloroauric acid (4 hydrate) were added to this emulsion per mol of silver, followed by heating at 75°C for 80 minutes to effect chemical sensitization. The thus obtained silver bromide grains were used as cores, and were allowed to further grow by adding a 2 mol/l sodium chloride aqueous solution and a 1 mol/l silver nitrate aqueous solution at 75°C for 40 minutes to obtain a cubic core/shell silver

chlorobromide emulsion of 0.6  $\mu\text{m}$  in average grain size (coefficient of variation: 15%). After washing with water and desalting of the emulsion, 0.5 mg of sodium thiosulfate was added thereto per mol of silver, then heated at 55°C for 60 minutes to effect chemical sensitization, whereby silver halide emulsion D was obtained.

#### Emulsion E

An aqueous solution of potassium bromide and an aqueous solution of silver nitrate were simultaneously added to a gelatin aqueous solution under vigorous stirring at 75°C over a period of 90 minutes to obtain a silver bromide emulsion containing octahedral grains of 0.8  $\mu\text{m}$  in average grain size (core grains). In the above procedure, before precipitation of silver halide grains of the emulsion 0.65 g of 3,4-dimethyl-1,3-thiazoline-2-thione was added to the aqueous gelatin solution and pH and pAg were maintained at 6 and 8.7 respectively during the step of precipitation. To the silver bromide emulsion were added 3.4 mg of sodium thiosulfate and 3.4 mg of potassium chloroaurate per mol of silver to effect chemical sensitization. The thus obtained chemically sensitized grains were allowed to further grow in the same precipitating environment as the core grain formation to finally obtain an octahedral core/shell silver bromide emulsion of 1.2  $\mu\text{m}$  in average grain size. Then,  $9.6 \times 10^{-4}$

mol of potassium iodide and  $4.2 \times 10^{-2}$  g of an N-vinylpyrrolidone polymer (weight-average molecular weight : 38,000) were added to the emulsion per mol of silver to obtain silver halide emulsion E.

#### Emulsion F

An aqueous solution of potassium bromide and an aqueous solution of silver nitrate were simultaneously added to a gelatin aqueous solution under vigorous stirring at 75°C over a period of 60 minutes to obtain a silver bromide emulsion. Before precipitation, 100 mg of 3,4-dimethyl-1,3-thiazoline-2-thione and 15 g of benzimidazole per mol of silver were added to a precipitation tank. After the completion of precipitation, crystals of 1.1  $\mu\text{m}$  in average grain size were obtained. Then, 5.4 mg of sodium thiosulfate and 3.9 mg of potassium chloroaurate were added to the emulsion per mol of silver, followed by heating at 75°C for 80 minutes to effect chemical sensitization. To the thus chemically sensitized core emulsion were added simultaneously an aqueous solution of potassium bromide and an aqueous solution of silver nitrate over a period of 40 minutes in the same manner as the first step to finally prepare a core/shell silver halide emulsion of 1.5  $\mu\text{m}$  in average grain size. Then, 0.32 mg of sodium thiosulfate and 57 mg of poly(N-vinylpyrrolidone) (weight-average molecular weight : 38,000) were added to the core/shell



emulsion per mol of silver, followed by heating at 60°C for 60 minutes to effect chemical sensitization on the surfaces of grains, whereby silver halide emulsion F was obtained.

#### Emulsion G

An aqueous solution of potassium bromide and an aqueous solution of silver nitrate were simultaneously added to a gelatin aqueous solution containing potassium bromide under vigorous stirring at 75°C over a period of about 60 minutes to obtain a silver bromide emulsion. Before precipitation (before the simultaneous addition), 150 mg of 3,4-dimethyl-1,3-thiazoline-2-thione as a silver halide solvent and 15 g of benzimidazole per mol of silver were added to the aqueous gelatin solution. After the completion of precipitation, uniform grain size octahedral silver bromide crystals of 0.8  $\mu\text{m}$  in average grain size were obtained. Then, 4.8 mg of sodium thiosulfate and 2.4 mg of potassium chloroaurate were added to the silver bromide emulsion per mol of silver, followed by heating at 75°C for 80 minutes to effect chemical sensitization. To the thus chemically sensitized inner nucleus (core) silver bromide emulsion were added simultaneously an aqueous solution of potassium bromide and an aqueous solution of silver nitrate over a period of 45 minutes in the same manner as the first step to precipitate internal latent image type core/shell emulsion. To the emulsion was added

2.5 g of hydrogen peroxide per mol of silver as an oxidizing agent, the emulsion was heated at 75°C for 8 minutes and then washed with water to obtain an emulsion of 1.0  $\mu\text{m}$  in average grain size (coefficient of variation : 12%). Then, to the internal latent image type core/shell silver bromide emulsion were added 0.75 mg of sodium thiosulfate and 20 mg of poly(N-vinylpyrrolidone) per mol of silver, followed by heating at 60°C for 60 minutes to effect chemical sensitization (ripening) on the surfaces of grains, whereby silver halide emulsion G was obtained.

#### Emulsion H

An aqueous solution of potassium bromide and an aqueous solution of silver nitrate were simultaneously added to a gelatin aqueous solution containing 0.3 g of 3,4-dimethyl-1,3-thiazoline-2-thione per mol of silver under vigorous stirring at 75°C over a period of 20 minutes to obtain a monodispersed silver bromide emulsion containing octahedral grains of 0.4  $\mu\text{m}$  in average grain size. 6 mg of sodium thiosulfate and 6 mg of chloroauric acid (4 hydrate) were added to the emulsion per mol of silver, followed by heating at 75°C for 80 minutes to effect chemical sensitization. The thus obtained silver bromide grains were used as cores, and were allowed to further grow in the same precipitating environment as the first step for 40 minutes to finally obtain an octahedral

monodispersed core/shell silver bromide emulsion of 0.7  $\mu$ m in average grain size. After washing with water and desalting of the emulsion, 1.5 mg of sodium thiosulfate and 1.5 mg of chloroauric acid (4 hydrate) were added thereto per mol of silver, followed by heating at 60°C for 60 minutes to effect chemical sensitization. Thus, internal latent image type silver halide emulsion H was obtained.

II) Preparation of Direct Positive Color  
Photographic Printing Paper

Using core/shell type direct positive emulsions A to H as described above, layers were coated on a reflective support composed of a vinyl chloride resin containing white pigments provided with subbing treatment as used in Example 1 to prepare a multilayer direct positive color photographic printing paper having the layer structure shown in Table 4 below. Coating solutions were prepared in the following manner.

Preparation of Coating Solution for First Layer

10 ml of ethyl acetate and 4 ml of solvent (c) were added to 6.4 g of Cyan Coupler (a) and 2.3 g of Color image stabilizer (b) to dissolve them, and the resulting solution was emulsified and dispersed in 90 ml of a 10% gelatin aqueous solution containing 5 ml of a 10% aqueous sodium dodecylbenzenesulfonate solution. On the other hand,  $2.0 \times 10^{-4}$  mol of a red-sensitizing dye shown below was added per mol of silver halide to the aforesaid silver

halide emulsion (containing 70 g of silver/kg) to prepare 90 g of a red-sensitive emulsion. The emulsified dispersion and the emulsion were mixed and dissolved, followed by adjusting the concentration of the dissolved mixture with addition of gelatin so as to become the composition as shown in Table 4 below. Further, 30 mg of Nucleating agent (n) and  $5 \times 10^{-4}$  mol of Nucleation accelerating agent (o) were added thereto per mol of silver to prepare a coating solution for the first layer.

Coating solutions for the second layer to the seventh layer were also prepared in the same manner as the coating solution for the first layer. Sodium salt of 1-hydroxy-3,5-dichloro-s-triazine was used as a gelatin hardener for each layer. Spectral sensitizers used for individual emulsions are shown below.

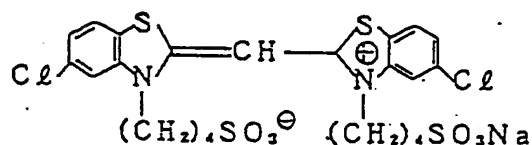
TABLE 4

<u>Layer</u>	<u>Main Composition</u>	<u>Amount Used</u>
7th Layer (Protective layer)	Gelatin	1.33 g/m <sup>2</sup>
	Acryl-modified poly-vinyl alcohol copolymer (modification degree: 17%)	0.17 g/m <sup>2</sup>
6th Layer (UV ray-absorbing layer)	Gelatin	0.54 g/m <sup>2</sup>
	UV ray absorbent (h)	$5.10 \times 10^{-4}$ mol/m <sup>2</sup>
	Solvent (j)	0.08 g/m <sup>2</sup>
5th Layer (Blue-sensitive layer)	Emulsion	0.40 g of Ag/m <sup>2</sup>
	Gelatin	1.35 g/m <sup>2</sup>
	Yellow coupler (k)	$6.91 \times 10^{-4}$ mol/m <sup>2</sup>

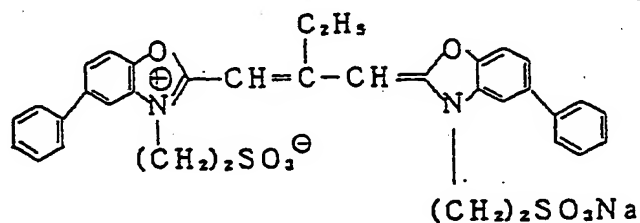
	Color image stabilizer (e)	0.13 g/m <sup>2</sup>
	Solvent (m)	0.02 g/m <sup>2</sup>
	Development controlling agent (x)	32 mg/m <sup>2</sup>
	Nucleating agent and Nucleating accelerating agent	
4th Layer (Intermediate layer)	Gelatin	1.60 g/m <sup>2</sup>
	Colloidal silver	0.10 g of Ag/m <sup>2</sup>
	UV ray absorbent (h)	$1.70 \times 10^{-4}$ mol/m <sup>2</sup>
	Color mixing preventing agent (i)	$1.60 \times 10^{-4}$ mol/m <sup>2</sup>
	Solvent (j)	0.24 g/m <sup>2</sup>
3rd Layer (Green-sensitive layer)	Emulsion	0.17 g of Ag/m <sup>2</sup>
	Gelatin	1.56 g/m <sup>2</sup>
	Magenta coupler (e)	$3.38 \times 10^{-4}$ mol/m <sup>2</sup>
	Color image stabilizer (f)	0.19 g/m <sup>2</sup>
	Solvent (g)	0.59 g/m <sup>2</sup>
	Development Controlling agent (x)	32 mg/m <sup>2</sup>
	Nucleating agent and Nucleating accelerating agent	
2nd Layer (Intermediate layer)	Gelatin	0.90 g/m <sup>2</sup>
	Color mixing preventing agent (d)	$2.33 \times 10^{-4}$ mol/m <sup>2</sup>
1st Layer (Red Sensitive layer)	Emulsion	0.39 g of Ag/m <sup>2</sup>
	Gelatin	0.90 g/m <sup>2</sup>
	Cyan coupler (a)	$7.05 \times 10^{-4}$ mol/m <sup>2</sup>
	Color image stabilizer (b)	$5.20 \times 10^{-4}$ mol/m <sup>2</sup>

Solvent (c)	0.22 g/m <sup>2</sup>
Development controlling agent (x)	32 mg/m <sup>2</sup>
Nucleating agent and Nucleation accelerating agent	
Support	Reflective support composed of a vinyl chloride resin containing white pigments provided with subbing treatment

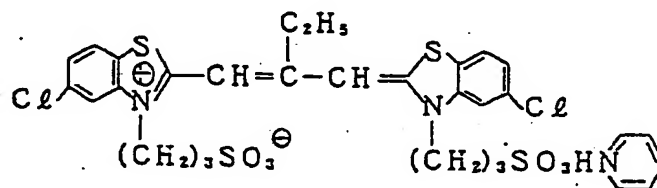
## Blue-Sensitive Emulsion Layer:



## Green-Sensitive Emulsion Layer:

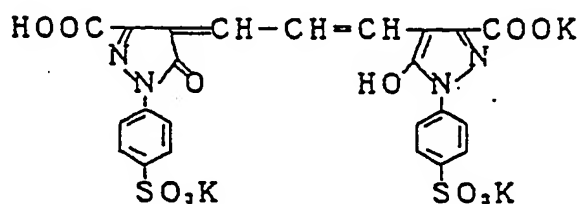


## Red-Sensitive Emulsion Layer:

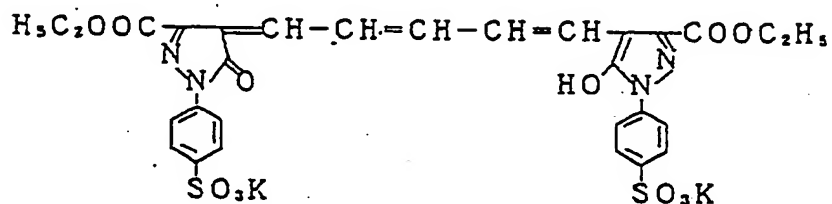


The following dyes were employed as irradiation preventing dyes in the emulsion layers, respectively.

Green-Sensitive Emulsion Layer:

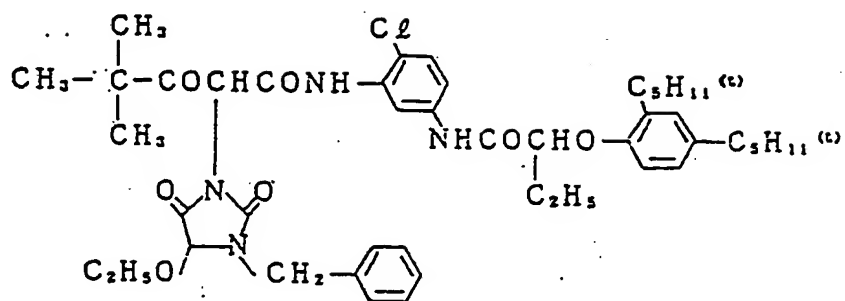


Red-Sensitive Emulsion Layer:

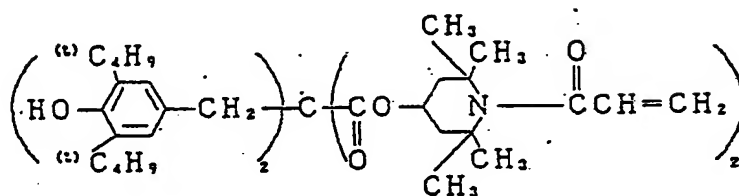


The chemical structures of the compounds such as couplers employed in this example are shown below.

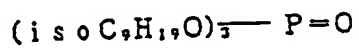
Yellow couper (k)



Color image stabilizer (l)

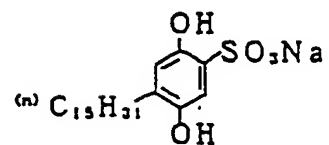


Solvent (m)

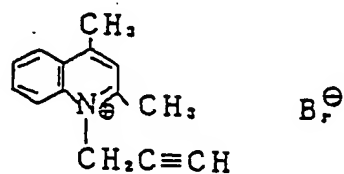




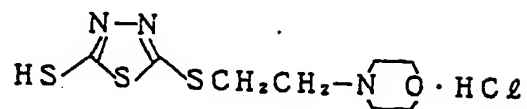
Development controlling agent (x)



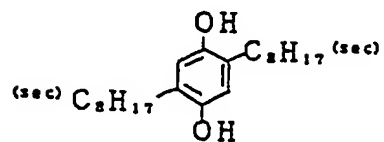
Nucleating agent (n)



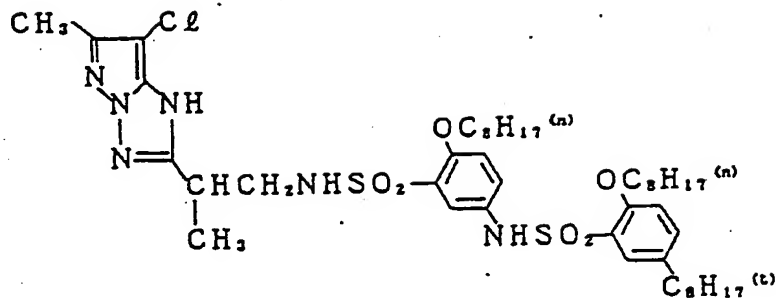
Nucleation accelerating agent (o)



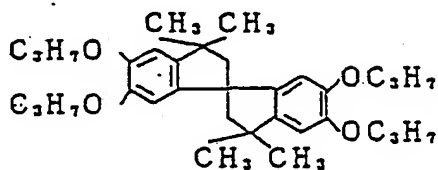
Color mixing preventing agent (d)



Magenta coupler (e)

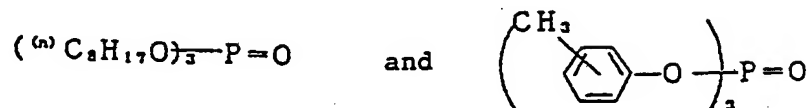


Color image stabilizer (f)



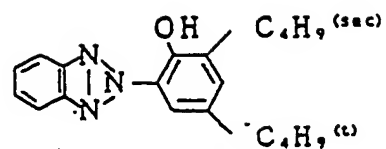
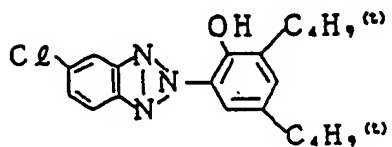
Solvent (g)

a mixture (2:1 by weight ratio) of

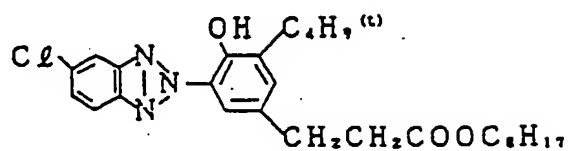


UV ray absorbent (h)

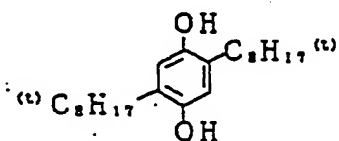
a mixture (1:5:3 by molar ratio) of



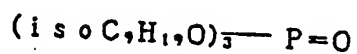
and



Color mixing preventing agent (i)

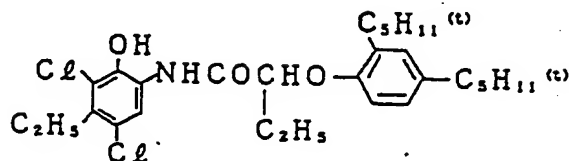


Solvent (j)

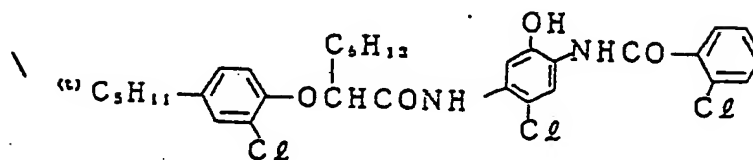


## Cyan coupler (a)

a mixture (1:1 by molar ratio) of

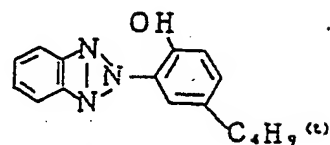
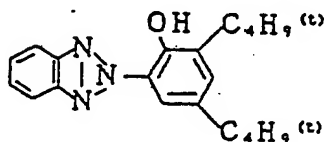


and

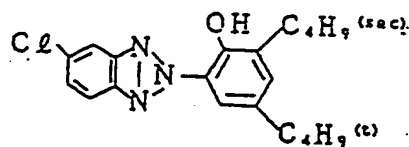


## Color image stabilizer (b)

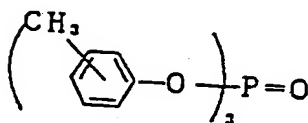
a mixture (1:3:3 by molar ratio) of



and



## Solvent (c)



The coating solutions for the first layer to the seventh layer were coated after adjusting the balance of surface tension and viscosity thereof simultaneously on the support to prepare multilayer silver halide direct positive color photographic printing paper A to H.

### III) Development Processing

The direct positive color photographic printing paper A to H thus prepared were imagewise exposed at color temperature of 4,800°K in an amount of 100 CMS at 1/10 second and then subjected to Processing Step A (pH of the color developing solution: 10.2) shown below and Processing Step B (same as Processing Step A except adjusting pH of the color developing solution to 11.0), respectively. Direct positive color photographic prints having excellent sharpness and no irregularity of image density were obtained.

#### Processing Step A:

<u>Step</u>	<u>Time</u>	<u>Temperature</u>
Color Development	2 min 30 sec	38°C
Bleach-fixing	40 sec	38°C
Stabilizing (1)	20 sec	38°C
Stabilizing (2)	20 sec	38°C
Stabilizing (3)	20 sec	38°C

The stabilizing baths were replenished according to a so-called countercurrent replenishing system of adding the replenisher to stabilizing bath (3),

introducing the overflow from the stabilizing bath (3) into stabilizing bath (2), and the overflow from the stabilizing bath (2) into stabilizing bath (1).

The composition of each processing solution used in the above described processing steps is as follows:

<u>Color Developing Solution:</u>	<u>Mother Solution</u>
Diethylenetriaminepentaacetic acid	2.0 g
Benzyl alcohol	12.8 g
Diethylene glycol	3.4 g
Sodium sulfite	2.0 g
Sodium bromide	0.26 g
Hydroxylamine sulfate	2.60 g
Sodium chloride	3.20 g
3-Methyl-4-amino-N-ethyl-N-( $\beta$ -methanesulfonamidoethyl)aniline	4.25 g
Potassium carbonate	30.0 g
Brightening agent (stilbene type)	1.0 g
Water to make	1,000 ml
pH	10.20

The pH was adjusted with potassium hydroxide or hydrochloric acid.

<u>Bleach-Fixing Solution:</u>	<u>Mother Solution</u>
Ammonium thiosulfate	110 g
Sodium hydrogensulfite	10 g
Ammonium iron (III) diethylene-triaminepentaacetate monohydrate	56 g

Disodium ethylenediaminetetra- acetate dihydrate	5 g
2-Mercapto-1,3,4-triazole	0.4 g
Water to make	1,000 ml
pH	6.5

The pH was adjusted with aqueous ammonia or hydrochloric acid.

Stabilizing solution:

Mother Solution

1-Hydroxyethylidene-1,1'-di phosphonic acid (60%)	1.6 ml
Bismuth chloride	0.35 g
Polyvinylpyrrolidone	0.25 g
Aqueous ammonia	2.5 ml
Trisodium nitrilotriacetate	1.0 g
5-Chloro-2-methyl-4-isothiazolin- 3-one	50 mg
2-Octyl-4-isothiazolin-3-one	50 mg
Brightening agent (4,4'-diamino-stilbene type)	1.0 g
Water to make	1,000 ml
pH	7.5

The pH was adjusted with potassium hydroxide or hydrochloric acid.

EXAMPLE 4

The first layer to the eleventh layer as described in Example 1 of Japanese Patent Application (OPI) No. 174760/87; pages 18, upper half portion in the right-hand column to page 21, lower half portion in the right-hand

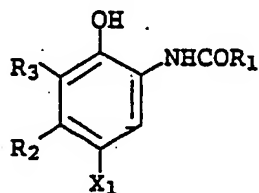
column were coated on a reflective support composed of a vinyl chloride resin containing white pigments provided with subbing treatment in place of the first layer to the seventh layer to prepare a reversal color photographic light-sensitive material. The color photographic material was processed according to the prescribed development processing steps. A reversal color photographic print having excellent sharpness and no irregularity of image density was obtained.

While the invention has been described in detail and with reference to specific embodiments thereof, it will be apparent to one skilled in the art that various changes and modifications can be made therein without departing from the spirit and scope thereof.

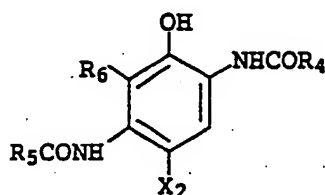


## WHAT IS CLAIMED IS:

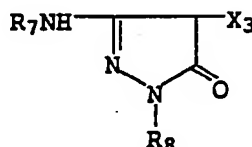
1. A silver halide color photographic material comprising a reflective support composed of a vinyl chloride resin containing a white pigment and having thereon in an appropriate order at least one red-sensitive silver halide emulsion layer containing a cyan color forming coupler represented by the general formula (1) or (2) shown below, at least one green-sensitive silver halide emulsion layer containing a magenta color forming coupler represented by the general formula (3) or (4) shown below, and at least one blue-sensitive silver halide emulsion layer containing a yellow color forming coupler represented by the general formula (5) shown below



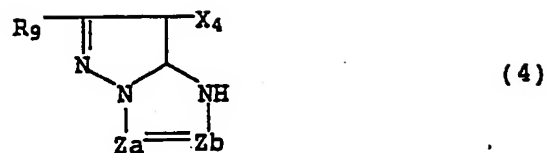
(1)



(2)



(3)



wherein R<sub>1</sub>, R<sub>4</sub> and R<sub>5</sub> each represents an aliphatic group, an aromatic group, a heterocyclic group, an aromatic amino group or a heterocyclic amino group; R<sub>2</sub> represents an aliphatic group; R<sub>3</sub> and R<sub>6</sub> each represents a hydrogen atom, a halogen atom, an aliphatic group, an aliphatic oxy group or an acylamino group; R<sub>7</sub> and R<sub>8</sub> each represents a substituted or unsubstituted phenyl group; R<sub>9</sub> represents a hydrogen atom or a substituent; R<sub>2</sub> and R<sub>3</sub> or R<sub>5</sub> and R<sub>6</sub> may be connected with each other to form a 5-membered to 7-membered ring; Q represents a substituted or unsubstituted N-phenylcarbamoyl group; Z<sub>a</sub> and Z<sub>b</sub>, which may be the same or different, each represents a group of -CH=, a

group of  $\begin{array}{c} R_{10} \\ | \\ -C= \end{array}$  or a group of  $-N=$ ;  $R_{10}$  represents the same substituent as that represented by  $R_9$ ; and  $X_1, X_2, X_3, X_4$  and  $X_5$  each represents a hydrogen atom or a group capable

of being released upon a reaction with an oxidation product of an aromatic primary amine developing agent.

2. A silver halide color photographic material as claimed in Claim 1, wherein  $X_1$  and  $X_2$  each represents a chlorine atom,  $X_3$  and  $X_4$  each represents a hydrogen atom or a group capable of being released containing a sulfur atom as a releasing atom; and  $X_5$  represents a group capable of being released containing an oxygen atom or a nitrogen atom as a releasing atom.

3. A silver halide color photographic material as claimed in Claim 1, wherein the vinyl chloride resin is a copolymer containing a vinyl chloride monomer.

4. A silver halide color photographic material as claimed in Claim 3, wherein the vinyl chloride monomer occupies at least 50% by weight of the total monomer component.

5. A silver halide color photographic material as claimed in Claim 3, wherein a comonomer component is selected from methyl methacrylate, vinyl acetate, acrylonitrile, a fluorinated olefin, a vinyl ether, vinyl bromide, vinyl acetate, maleic acid, dichlorobutadiene, vinyl fluoride, vinylidene fluoride, trifluorochloroethylene, tetrafluoroethylene, vinylidene chloride, acrylonitrile, styrene, butadiene, and chloroprene.

6. A silver halide color photographic material as claimed in Claim 1, wherein the white pigment is

selected from titanium white, zinc white, calcium carbonate, barium sulfate, white lead, white organic pigments and dyes, and brightening agents.

7. A silver halide color photographic material as claimed in Claim 1, wherein the total amount of the white pigment added is from 1 part by weight to 30 parts by weight per 100 parts by weight of the vinyl chloride resin material.

8. A silver halide color photographic material as claimed in Claim 1, wherein an average reflectivity of the reflective support in a visible range is from 80 to 98%.

9. A silver halide color photographic material as claimed in Claim 1, wherein the thickness of the reflective support is from 50  $\mu\text{m}$  to 500  $\mu\text{m}$ .

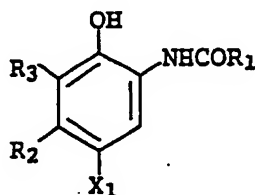
10. A silver halide color photographic material as claimed in Claim 1, wherein a surface of the reflective support to which a hydrophilic colloid layer is applied is subjected to subbing treatment.

11. A silver halide color photographic material as claimed in Claim 1, wherein the color photographic material further comprises a development inhibitor releasing compound.

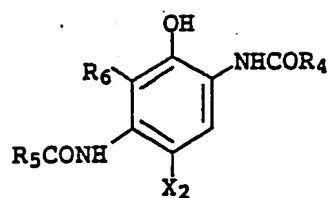
12. A silver halide color photographic material as claimed in Claim 1, wherein a silver halide emulsion

used in the silver halide emulsion layers is a mono-dispersed silver halide emulsion.

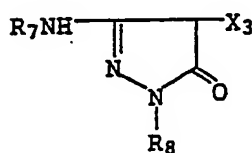
13. A color photographic print comprising a reflective support composed of a vinyl chloride resin containing a white pigment and having thereon in an appropriate order at least one emulsion layer containing a cyan dye obtained by a reaction of a cyan color forming coupler represented by the general formula (1) or (2) shown below with an oxidation product of an aromatic primary amine developing agent, at least one emulsion layer containing a magenta dye obtained by a reaction of a magenta color forming coupler represented by the general formula (3) or (4) shown below with an oxidation product of an aromatic primary amine developing agent, and at least one emulsion layer containing a yellow dye obtained by a reaction of a yellow color forming coupler represented by the general formula (5) shown below with an oxidation product of an aromatic primary amine developing agent



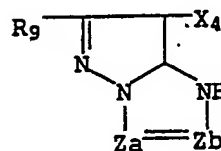
(1)



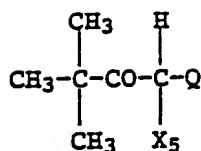
(2)



(3)



(4)



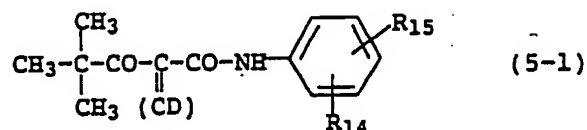
(5)

wherein  $R_1$ ,  $R_4$  and  $R_5$  each represents an aliphatic group, an aromatic group, a heterocyclic group, an aromatic amino group or a heterocyclic amino group;  $R_2$  represents an aliphatic group;  $R_3$  and  $R_6$  each represents a hydrogen atom, a halogen atom, an aliphatic group, an aliphatic oxy group or an acylamino group;  $R_7$  and  $R_8$  each represents a substituted or unsubstituted phenyl group;  $R_9$  represents

a hydrogen atom or a substituent;  $R_2$  and  $R_3$  or  $R_5$  and  $R_6$  may be connected with each other to form a 5-membered to 7-membered ring;  $Q$  represents a substituted or unsubstituted N-phenylcarbamoyl group;  $Za$  and  $Zb$ , which may be the same or different, each represents a group of  $-CH=$ , a

group of  $\overset{R_{10}}{\underset{|}{-C=}}$  or a group of  $-N=$ ;  $R_{10}$  represents the same substituent as that represented by  $R_9$ ; and  $X_1$ ,  $X_2$ ,  $X_3$ ,  $X_4$  and  $X_5$  each represents a hydrogen atom or a group capable of being released upon a reaction with an oxidation product of an aromatic primary amine developing agent.

14. A color photographic print as claimed in Claim 13, wherein the yellow dye is a dye represented by the following general formula (5-1):



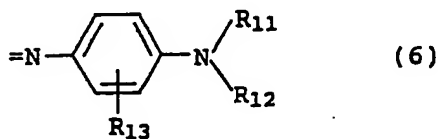
wherein  $R_{14}$  and  $R_{15}$ , which may be the same or different, each represents a hydrogen atom or a substituent which is ordinarily used for a yellow coupler, provided that both  $R_{14}$  and  $R_{15}$  are not hydrogen atoms at the same time; and

$\text{(CD)}$  represents a coupling residue of an aromatic primary amine developing agent.

15. A color photographic print as claimed in Claim 14, wherein the substituent represented by  $R_{14}$  or

R<sub>15</sub> is selected from an alkyl group, an alkenyl group, an alkoxy group, an alkoxycarbonyl group, a halogen atom, an alkoxy carbamoyl group, an aliphatic amido group, an alkylsulfamoyl group, an alkylsulfonamido group, an alkylureido group, an alkyl-substituted succinimido group, an aryloxy group, an aryloxy carbonyl group, an arylcarbamoyl group, an arylamido group, an arylsulfamoyl group, an arylsulfonamide group, an arylureido group, a carboxy group, a sulfo group, a nitro group, a cyano group and a thiocyano group.

16. A color photographic print as claimed in Claim 14, wherein  $\begin{array}{c} \parallel \\ \text{(CD)} \end{array}$  represents a coupling residue of a phenylenediamine derivative represented by the following general formula (6):

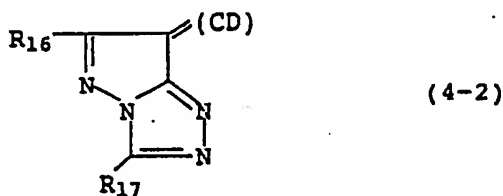
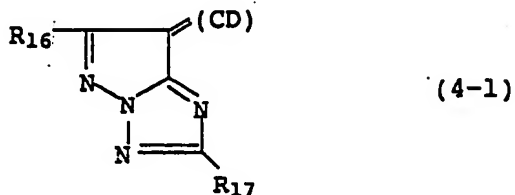


wherein R<sub>11</sub> and R<sub>12</sub> each represents a substituted or unsubstituted alkyl group; and R<sub>13</sub> represents one to four hydrogen atoms or one to four substituents.

17. A color photographic print as claimed in Claim 16, wherein a substituent for the substituted alkyl group represented by R<sub>11</sub> or R<sub>12</sub> is selected from a hydroxy group, an alkylsulfonamido group and an alkoxy group, and the substituent represented by R<sub>13</sub> is an alkyl group.



18. A color photographic print as claimed in Claim 13, wherein the magenta dye is a dye represented by the following general formula (4-1) or (4-2):



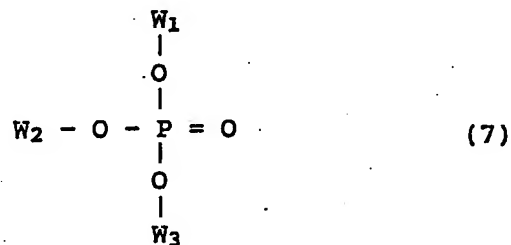
wherein  $R_{16}$  and  $R_{17}$ , which may be the same or different, each represents a hydrogen atom, a halogen atom, an alkyl group, an aryl group, a heterocyclic group, a cyano group, an alkoxy group, an aryloxy group, a heterocyclic oxy group, an acyloxy group, a carbamoyloxy group, a silyloxy group, a sulfonyloxy group, an acylamino group, an anilino group, a ureido group, an imido group, a sulfamoylamino group, a carbamoylamino group, an alkylthio group, an arylthio group, a heterocyclic thio group, an alkoxy-carbonylamino group, an aryloxy-carbonylamino group, a sulfonamido group, a carbamoyl group, an acyl group, a sulfamoyl group, a sulfonyl group, a sulfinyl group, an

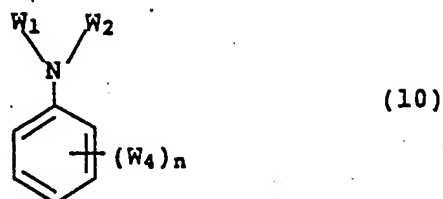
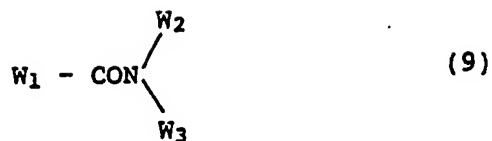
alkoxycarbonyl group or an aryloxycarbonyl group, or  $R_{16}$  or  $R_{17}$  may be a divalent group to form a bis compound or a linking group to form a polymer dye, and  $\text{CD}$  represents a coupling residue of an aromatic primary amine developing agent.

19. A color photographic print as claimed in Claim 18, wherein the linking group is connected to a vinyl group from which the polymer is formed.

20. A color photographic print as claimed in Claim 13, wherein the cyan dye is composed of two or more dyes formed from two or more cyan color forming couplers represented by the general formula (1) or (2).

21. A color photographic print as claimed in Claim 13, wherein the dyes are used in combination with one or more kinds of organic solvents having a high boiling point of at least  $160^{\circ}\text{C}$  represented by the following general formula (7), (8), (9), (10) or (11):



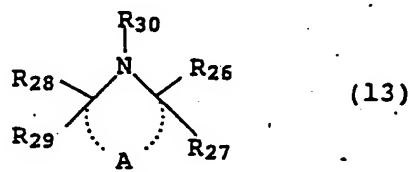
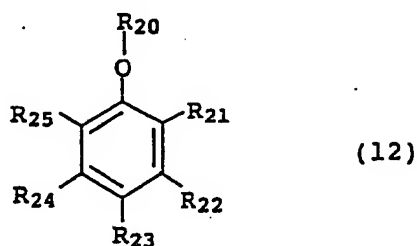


wherein  $W_1$ ,  $W_2$  and  $W_3$  each represents a substituted or unsubstituted alkyl group, a substituted or unsubstituted cycloalkyl group, a substituted or unsubstituted alkenyl group, a substituted or unsubstituted aryl group or a substituted or unsubstituted heterocyclic group;  $W_4$  represents  $W_1$ ,  $-O-W_1$  or  $-S-W_1$ ;  $n$  represents an integer from 1 to 5, when  $n$  is two or more, two or more  $W_4$ 's may be the same or different; and  $W_1$  and  $W_2$  in the general formula (11) may be connected with each other to form a condensed ring.

22. A color photographic print as claimed in Claim 13, wherein the dyes are used in combination with

one or more kinds of water-insoluble, organic solvent-soluble polymers.

23. A color photographic print as claimed in Claim 13, wherein the dyes are used in combination with one or more kinds of color fading preventing agents or antioxidants represented by the following general formula (12) or (13):



wherein R<sub>20</sub> represents a hydrogen atom, an aliphatic group, an aromatic group, a heterocyclic group or a hydrolyzable protective group; R<sub>21</sub>, R<sub>22</sub>, R<sub>23</sub>, R<sub>24</sub> and R<sub>25</sub>, which may be the same or different, each represents a hydrogen atom or a substituent; R<sub>30</sub> represents a hydrogen atom, an aliphatic group, an acyl group, a sulfonyl group, a sulfinyl group, an oxy radical group or a hydroxy group; A represents a non-metallic atomic group necessary to form a 5-membered, 6-membered or 7-membered ring; and R<sub>26</sub>, R<sub>27</sub>, R<sub>28</sub> and R<sub>29</sub>, which may be the same or different, each

represents a hydrogen atom or an alkyl group, or R<sub>20</sub> and R<sub>21</sub> or two of R<sub>21</sub>, R<sub>22</sub>, R<sub>23</sub>, R<sub>24</sub> and R<sub>25</sub> which are present in ortho-positions with respect to each other may be connected with each other to form a 5-membered, 6-membered or 7-membered ring, or R<sub>26</sub> and R<sub>27</sub>, R<sub>28</sub> and R<sub>29</sub> or R<sub>30</sub> and R<sub>26</sub> may be connected with each other to form a 5-membered, 6-membered or 7-membered ring.

24. A color photographic print prepared by conducting at least a step of processing the silver halide color photographic material as claimed in Claim 1, after imagewise exposure, with a color developing solution containing an aromatic primary amine color developing agent.

25. A color photographic print prepared by adhering a color photographic print obtained by conducting at least a step of processing the silver halide color photographic material as claimed in Claim 1 except using a transparent support instead of the reflective support, after imagewise exposure, with a color developing solution containing an aromatic primary amine color developing agent, on a reflective support composed of a vinyl chloride resin containing a white pigment.

**EUROPEAN PATENT APPLICATION**

Application number: 87117764.8

Int. Cl.<sup>5</sup>: G03C 1/78, G03C 7/32

Date of filing: 01.12.87

Priority: 02.12.86 JP 287456/86  
20.04.87 JP 95440/87

Date of publication of application:  
08.06.88 Bulletin 88/23

Designated Contracting States:  
DE FR GB NL

Date of deferred publication of the search report:  
16.08.90 Bulletin 90/33

Applicant: Fuji Photo Film Co., Ltd.  
210 Nakanuma Minamishigara-shi  
Kanagawa-ken(JP)

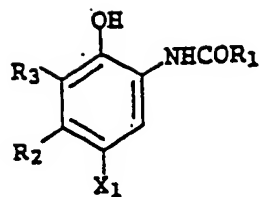
Inventor: Aogaki, Yukio Fuji Photo Film Co.,  
Ltd.  
No. 210 Nakanuma  
Minamishigara-shi Kanagawa-ken(JP)  
Inventor: Toda, Yuzo Fuji Photo Film Co., Ltd.  
No. 210 Nakanuma  
Minamishigara-shi Kanagawa-ken(JP)  
Inventor: Minagawa, Nobuhiko Fuji Photo Film  
Co., Ltd.  
No. 210 Nakanuma  
Minamishigara-shi Kanagawa-ken(JP)

Representative: Patentanwälte Grünecker,  
Kinkeldey, Stockmair & Partner  
Maximilianstrasse 58  
D-8000 München 22(DE)

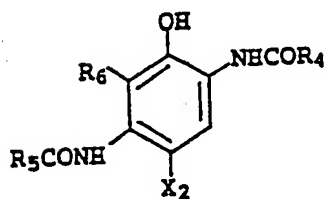
**Silver halide color photographic material and color photographic print.**

A silver halide color photographic material is described, comprising a reflective support composed of a vinyl chloride resin containing a white pigment and having thereon in an appropriate order at least one red-sensitive silver halide emulsion layer containing a cyan color forming coupler represented by the general formula (1) or (2) shown below, at least one green-sensitive silver halide emulsion layer containing a magenta color forming coupler represented by the general formula (3) or (4) shown below, and at least one blue-sensitive silver halide emulsion layer containing a yellow color forming coupler represented by the general formula (5) shown below

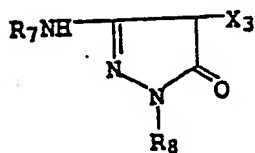
**EP 0 270 078 A3**



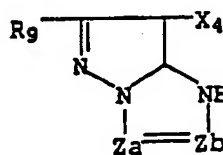
(1)



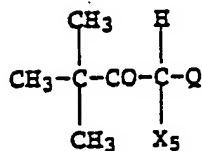
(2)



(3)



(4)



(5)

wherein  $R_1$ ,  $R_4$  and  $R_5$  each represents an aliphatic group, an aromatic group, a heterocyclic group, an aromatic amino group or a heterocyclic amino group;  $R_2$  represents an aliphatic group;  $R_3$  and  $R_6$  each represents a hydrogen atom, a halogen atom, an aliphatic group, an aliphatic oxy group or an acylamino group;  $R_7$  and  $R_8$  each represents a substituted or unsubstituted phenyl group;  $R_9$  represents a hydrogen atom or a substituent;  $R_2$  and  $R_3$  or  $R_5$  and  $R_6$  may be connected with each other to form a 5-membered to 7-membered ring;  $Q$  represents a substituted or unsubstituted N-phenylcarbamoyl group;  $Za$  and  $Zb$ , which may be the same or different, each represents a group of  $-CH=$ , a group of



or a group of  $-N=$ ;  $R_{10}$  represents the same substituent as that represented by  $R_9$ ; and  $X_1$ ,  $X_2$ ,  $X_3$ ,  $X_4$  and

X<sub>S</sub> each represents a hydrogen atom or a group capable of being released upon a reaction with an oxidation product of an aromatic primary amine developing agent.

The silver halide color photographic material provides a color photographic print having color images of excellent sharpness and good smoothness.

A color photographic print comprising a reflective support composed of a vinyl chloride resin containing a white pigment and having thereon in an appropriate order at least one emulsion layer containing a cyan dye obtained by a reaction of a cyan color forming coupler represented by the general formula (1) or (2) shown above with an oxidation product of an aromatic primary amine developing agent (CD), at least one emulsion layer containing a magenta dye obtained by a reaction of a magenta color forming coupler represented by the general formula (3) or (4) shown above with a CD, and at least one emulsion layer containing a yellow dye obtained by a reaction of a yellow color forming coupler represented by the general formula (5) shown above with a CD is also described.





European Patent  
Office

# EUROPEAN SEARCH REPORT

Application Number

EP 87 11 7764

DOCUMENTS CONSIDERED TO BE RELEVANT			
Category	Citation of document with indication, where appropriate, of relevant passages	Relevant to claim	CLASSIFICATION OF THE APPLICATION (Int. Cl.4)
Y, D	EP-A-0065329 (AGFA-GEVAERT) * page 4, lines 1 - 17 * * page 6, lines 21 - 24 * * page 7, lines 29 - 34; claim 1 *	1-25	G03C1/78 G03C7/32
Y	EP-A-0162328 (FUJI) * page 51, line 10 - page 52, line 22 * * page 54, lines 11 - 15 * * page 65, line 15 - page 67, line 8 * * page 91, lines 8 - 10 * * page 103 * * page 125, line 3; claim 1 *	1-25	
Y	US-A-4120725 (NAKAZYO ET AL.) * column 11, lines 49 - 59 * * column 12, line 46 - column 15, line 10; claim 1 *	1-25	
Y	EP-A-0164961 (KODAK) * page 5, line 23 - page 13, line 17 * * page 23, line 17 - page 24, line 3 * * page 28, lines 10 - 33 *	1-25	TECHNICAL FIELDS SEARCHED (Int. Cl.4)
A	FR-A-2245616 (BASF) * page 1, line 38 - page 2, line 20 *	21	G03C
The present search report has been drawn up for all claims			
Place of search THE HAGUE		Date of completion of the search 12 JUNE 1990	Examiner MAGRIZOS S.
<b>CATEGORY OF CITED DOCUMENTS</b> X : particularly relevant if taken alone Y : particularly relevant if combined with another document of the same category A : technological background O : non-written disclosure P : intermediate document T : theory or principle underlying the invention E : earlier patent document, but published on, or after the filing date D : document cited in the application L : document cited for other reasons * : member of the same patent family, corresponding document			

**THIS PAGE BLANK (USPTO)**